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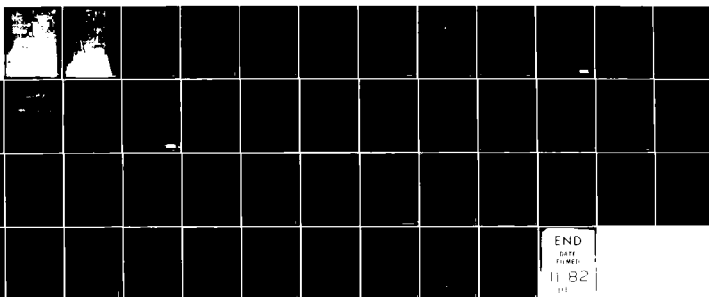
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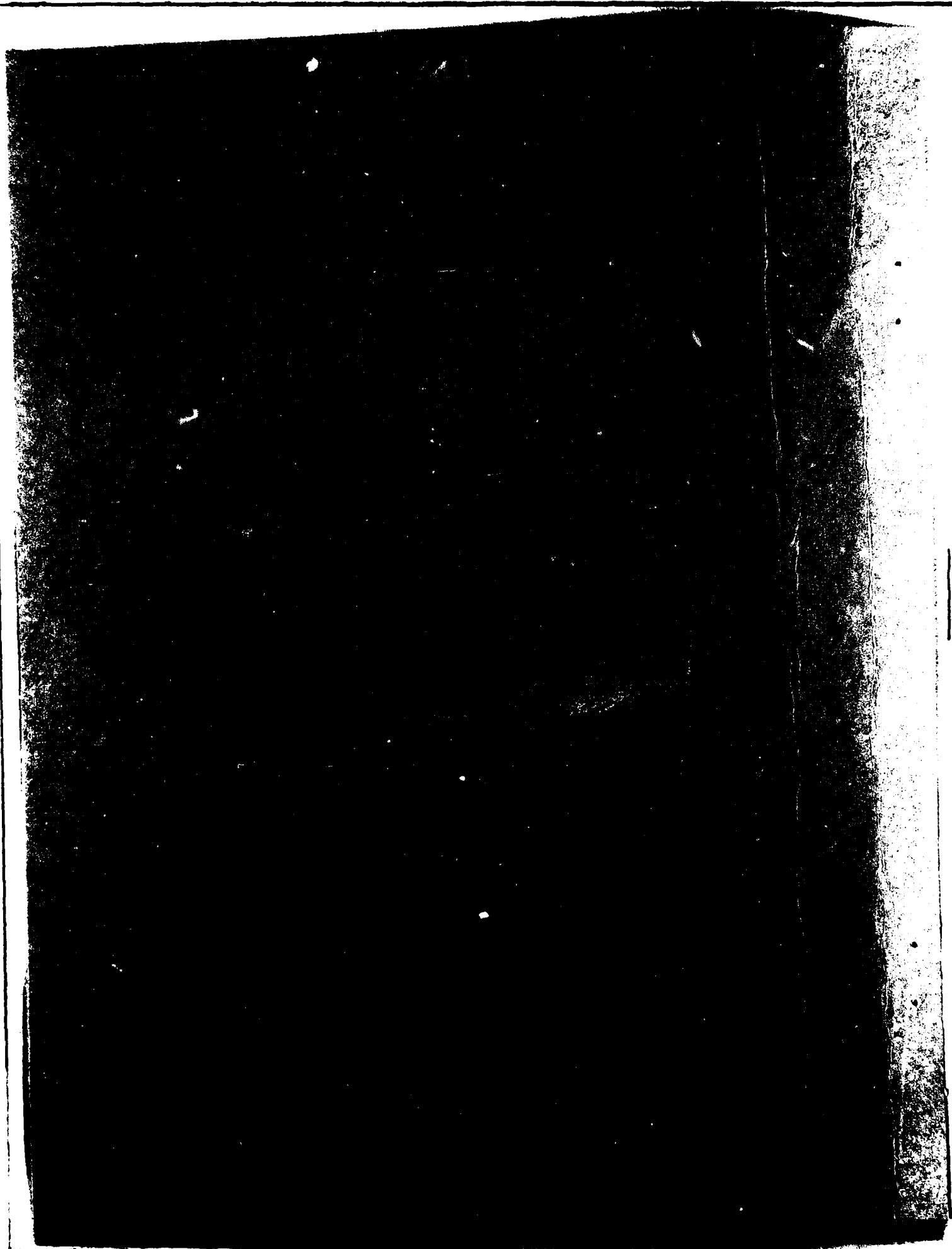
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The present Scientific Report is assembled with three technical papers, two of them published and one submitted for publication, during the first year of the contract. They are

- (i) "The 5g Levels of Atomic Nitrogen" *AD-A119 508*

Edward S. Chang and Hajime Sakai
J. Phys. B 14, L391 (1981)

- (ii) "Infrared Emission Spectroscopy of Glow Discharge Formed in Low Pressure Atmospheric Gases" *AD-A119 509*

H. Sakai, P. Hansen, M. Esplin, R. Johansson, M. Peltola, and J. Strong
Appl. Opt. 21, 228 (1982)

- (iii) "A New Rotation-Vibration Hamiltonian"

L.S. Mayants
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LETTER TO THE EDITOR

The 5g levels of atomic nitrogen

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Received 27 February 1981

Abstract. Energy levels and relative strengths for the 4f-5g transition in N I are calculated in the $j-l$ coupling scheme. Excellent agreement is found with our interferometric data from $\sigma = 2455$ to 2505 cm^{-1} in both positions and intensities.

5g m.f.
The 5g levels in atoms are usually determined from measurements of the 4f-5g lines. Spectroscopic studies were performed on closed-core atoms such as the alkali metals (Litzen 1970a) and on helium (Litzen 1970b). However, other atoms were not studied, apparently because of the expected complications in the term analysis due to an open core, and in detecting low-intensity atomic emissions among molecular bands.

In this letter, we show that the 5g levels of N I (which has an open core) are accurately described by $j-l$ coupling (i.e., in the $jLK M_K$ scheme). This coupling ignores the spin of the Rydberg electron and is an approximation to $j-K$ coupling (i.e., the jKM_J scheme) employed, for example, in Ti III (Edlén and Svensson 1975, Goldschmidt 1981). The resulting simplification allows the analytic calculation of the relative line strengths for the 4f-5g transition. This theoretical analysis enables us to identify our glow discharge interferometric data in nitrogen (mixed with helium) from 2455 to 2505 cm^{-1} as 4f-5g emission lines in N I. These atomic lines lie in the same spectral region as the molecular W-B (4, 2) band observed by Benesch and Saum (1971) under different discharge conditions.

The general theory of coupling between an open core and Rydberg electron with high orbital angular momentum has been described by Shortley and Fried (1938) and by Racah (1942a, b). In application to nf and ng in N II (Eriksson 1956) and to nf in the isoelectronic O II (Eriksson 1961), it was noted that the spin of the Rydberg electron s was in effect decoupled from the rest of the system. Consequently, the system can be described in $L-S$, in $j-l$, or generally in the intermediate coupling scheme (called pair coupling).

To expedite the calculation of line strengths, we work entirely in the $j-l$ coupling scheme. Since the electrostatic energies are usually given in a coupling scheme resulting in total orbital angular momentum L , we apply the transformation to $j-l$ coupling given by

$$[(\langle L_c \rangle L, S_c | l, \langle L_c S_c \rangle) f]^{(K)} = (-1)^{l+L_c+S_c+K} [(2l+1)(2j+1)]^{1/2} \begin{Bmatrix} l & L_c & L \\ S_c & K & j \end{Bmatrix}. \quad (1)$$

In equation (1) L_c , S_c , and j refer respectively to the orbital, spin and total angular momenta of the core, and l and L are the orbital angular momenta of the Rydberg

electron and the entire atom. K is the invariant angular momentum, ignoring s . Retaining only F_2 of the electrostatic energies given by Racah (1942a):

$$(LS_c|E|LS_c) = F_2(2p, nl) \times \begin{cases} -l(2l-1) & \text{for } L = l+1 \\ (2l-1)(2l+3) & L = l \\ -(l+1)(2l+3) & L = l-1 \end{cases} \quad (2)$$

we find the energy in j - l coupling to be given by

$$E_{LK} = \sum_L (2L+1)(2j+1) \begin{Bmatrix} l & L_c & L \\ S_c & K & j \end{Bmatrix}^2 (LS_c|E|LS_c) \quad (3)$$

where

$$\begin{Bmatrix} j_1, j_2, j_3 \\ j_4, j_5, j_6 \end{Bmatrix}$$

are the 6- j symbols. Using standard Racah algebra, we obtain the line strength as

$$S(jlK, j'l'K') = \delta_{jj'} \delta_{KK'} (2K+1)(2K'+1) \begin{Bmatrix} K & K' & 1 \\ j & l & j \end{Bmatrix}^2 S_H \quad (4)$$

where $S_H = \langle l || P^{(1)} || l' \rangle^2 R_H^2$ are essentially the hydrogen line strengths, for a Rydberg electron with $l \geq 3$.

In application to N I, we have $L_c = S_c = 1$ for the ground core state $(2p)^2 {}^3P$, which splits into $j = 0, 1$ and 2 levels. Further splittings due to electrostatic interaction with the Rydberg electron are obtained from equation (3). The results for the 4f and the 5g configurations are given in table 1. In addition, line strengths given by equation (4) are shown for allowed transitions which obey $\Delta j = 0$ and $\Delta K = 0$ or ± 1 . In comparing relative strengths in H I, Bethe and Salpeter (1957) observed that the most intense lines are those with $\Delta n = \Delta l = -1$. Our results in table 1 and the more general results in

Table 1. Theoretical energies and line strengths of the 4f-5g transition.

l	K	$E_{3K}^\dagger$	$E_{4K}^\ddagger$	$S(jlK, j'l'K')^\S$				
				$K'=1$	2	3	4	5
0	3	0						
	4		0			1.00		
1	2	6						
	3	-7.5	27.5		0.71	0.06	0.00	
	4	2.5	-38.5			0.94	0.06	
	5		14				1.22	
2	1	-12						
	2	-3	-55	0.43	0.12	0.01		
	3	5.5	-5.5		0.60	0.17	0.01	
	4	7.5	32.5			0.82	0.18	0.01
	5	-5	35				1.10	0.12
	6		-28					1.44

† In units of $F_2(2p, 4f) = 1.861 \text{ cm}^{-1}$.

‡ In units of $F_2(2p, 5g) = 0.08667 \text{ cm}^{-1}$.

§ In units of S_H .

equation (4) enable us to extend their rule to a complex atom in $j-l$ coupling, i.e. the most intense lines are those with $\Delta K = \Delta n = \Delta l = -1$. As expected from properties of the $6-j$ symbols, the sum of the strengths for each value of j is $(2j+1)$. The values of the electrostatic interaction integrals for N I were calculated (Eriksson 1967) to be $F_2(2p, 4f) = 1.861 \text{ cm}^{-1}$ and $F_2(2p, 5g) = 0.08667 \text{ cm}^{-1}$. In the case of the $4f$ configurations, energy levels calculated from table 1 may differ from the experimental values by several cm^{-1} . However, for the $5g$ configuration F_2 is substantially smaller, so our approximation can be expected to be much better as we will see.

The infrared emission data analysed in the present study were generated in a 'Pfund' type optical cell 30 m long, and 1 m in diameter. At both ends were placed two concave mirrors of 30 m focal length. The glow discharge was formed between the wall of the optical cell and a 12 m long electrode placed at the central region. An AC 60 Hz voltage of 700 V RMS was applied to activate the discharge at the rate of 200 W. The source was a continuous flow type; a gas sample of a He-N₂ mixture was admitted at one end of the cell and pumped out at the other end at a constant rate. The pressure inside the

Table 2. Experimental energy levels of the $4f$ and the $5g$ configurations of N I.

j	K	$4f (\text{cm}^{-1})$	$5g (\text{cm}^{-1})$
0	3	110 349.11	
	4		112 834.03
1	2	110 404.50	
	3	110 385.30	112 885.10
	4	110 402.10	112 879.38
	5		112 883.97
2	1	110 459.76	
	2	110 485.98	112 960.07
	3	110 498.39	112 964.96†
	4	110 501.72	112 967.97‡
	5	110 473.37	112 968.38
	6		112 962.63

† Possibly $112\,965.29 \text{ cm}^{-1}$.

‡ Greater uncertainty due to He I line.

discharge chamber was maintained at approximately 0.1 Torr. The infrared radiation was admitted to an infrared interferometer placed at the exit port of the optical cell through a KBr lens. The experimental set-up was designed to achieve two objectives (i) the generation of a large number of infrared photons by forming a large glow discharge column; and (ii) optimum spectrometric efficiency realised by using the Fourier spectroscopy technique. The interferogram signal was detected by an InSb detector housed in a liquid N₂ Dewar. The path difference of the interferometer spectrometer was monitored by the interference fringe signal of the HeNe cw laser line 6328 Å . The spectrum used in the present analysis was produced with a resolution of 0.12 cm^{-1} . The accuracy for the present line position measurement was considerably higher than that obtained by the conventional spectrometer measurement, because each spectral line in our measurement was directly referenced to the HeNe laser line (15798.00 cm^{-1} in vacuum).

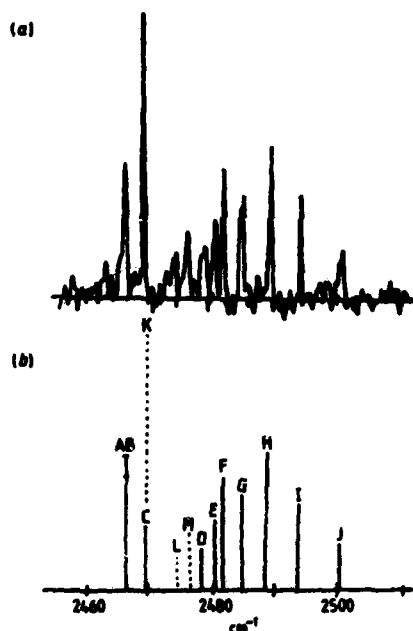


Figure 1. (a) Our observed spectrum between 2455 and 2505 cm^{-1} . (b) Theoretical intensities of N I are shown as full lines as follows. A: $j=2, K=3 \leftarrow 3$; B: $j=2, K=4 \leftarrow 5$; C: $j=2, K=3 \leftarrow 4$; D: $j=2, K=2 \leftarrow 3$; E: $j=1, K=2 \leftarrow 3$; F: $j=1, K=4 \leftarrow 5$; G: $j=0, K=3 \leftarrow 4$; H: $j=2, K=5 \leftarrow 6$; I: $j=1, K=3 \leftarrow 4$, and J: $j=2, K=1 \leftarrow 2$. In order to distinguish them from the N I spectrum, the following He I lines are shown as broken lines. K: $4f^1F \leftarrow 5g^1G$ and $4f^3F \leftarrow 5g^3G$; L: $4d^1D \leftarrow 5f^1F$ and M: $4d^3D \leftarrow 5f^3F$.

Figure 1(a) shows the emission intensity in a nitrogen-helium glow discharge. The most intense peak centred at $\sigma = 2469.58 \text{ cm}^{-1}$ is due to the $4f-5g$ line of He I as its relative value varies with the mixture ratio of He in several different runs. Note the significant discrepancy with the previously measured value of 2469.749 cm^{-1} (Litzen 1970b). We assign the next largest peak at 2489.26 cm^{-1} as the $4f-5g$ line ($j=2, K=5 \leftarrow 6$) of N I, which is the most intense as seen in table 1. From the experimental value of the $4f$ ($j=2, K=5$) level at $110\,473.37 \text{ cm}^{-1}$ labelled G(5) by Eriksson and Johansson (1961), we determine the energy of the $5g$ ($j=2, K=6$) level to be $112\,962.63 \text{ cm}^{-1}$. From table 1, the rest of the $5g$ levels can be calculated by adopting the experimental values for the $4f$ levels. The resulting positions and intensities ($\sigma^4 \times$ strengths) are shown in figure 1(b). The striking agreement between the two sets serves to identify the data unambiguously as the $4f-5g$ transitions of N I. Simultaneously, it verifies the validity of $j-l$ coupling for both the $4f$ and the $5g$ configurations. The theoretical $5g$ levels determined from table 1 differ from our measured values by only a few tenths of a wavenumber.

In conclusion, the $5g$ levels of N I have been identified for the first time and measured to an absolute accuracy of 0.01 cm^{-1} by infrared interferometry. The emission line intensities to the $4f$ levels are in excellent agreement with theory using the $j-l$ coupling scheme. The general expression for the line strength and the propensity rule $\Delta K = -1$ are applicable to other Rydberg states in any atom provided that $l \geq 3$.

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Infrared emission spectroscopy of glow discharge formed in low pressure atmospheric gases

H. Sakai, P. Hansen, M. Esplin, R. Johansson, M. Peltola, and J. Strong

Laboratory study was conducted on the molecular and atomic emissions which are considered detectable in the IR radiative background of the upper atmosphere. The IR spectra of glow discharge emission formed in air and other atmospheric constituent gases of 0.1-Torr pressure and a 30-m long column were surveyed using the technique of Fourier spectroscopy. Several features hitherto unobserved were detected in our survey study.

I. Introduction

Recently, in parallel with the advent of IR technology, various study efforts on IR emission revealed the atomic and molecular features poorly known in the past. In two specific areas of the observational studies, one for the atmospheric interest and another for the astrophysics interest, the spectroscopic data of the IR emission are obtained for situations which were considered impossible a decade ago. Most of the emission data currently obtained in field observations are those of a relatively low spectral resolution, causing the task of making unambiguous identification of the spectral feature found in the data rather difficult. A primary objective in the field observation study is concerned with physical and chemical processes involved in the emission mechanism. It cannot be achieved unless a proper identification can be assigned to the observed spectral feature. Under the circumstances where the field data are provided with a spectral resolution insufficient for producing a clear spectral identification, a laboratory spectroscopic study on the candidate atomic and molecular IR emission provides worthwhile assistance to the analysis effort. Our study effort was made in part to fulfill the need called for in such a circumstance. We collected the data on the IR emission feature of atmospheric species, atoms, and molecules, with a moderate spectral resolution using the technique of Fourier spectroscopy, and studied them.

The primary interest of our study was focused on the region of the upper atmosphere above 60 km, where the pressure remains below 1 Torr. The measurement efforts for the IR emission in the upper atmosphere were summarized in a recent review article by Baker *et al.*¹ The IR emission generated by the electrons of 20–30 eV exciting the atmospheric molecules was our main study subject. Our basic experimental approach to the study was twofold: (1) by forming a large electric glow discharge column, the IR photons of various atmospheric species were produced in a large quantity; and (2) by using Fourier multiplex spectroscopy, the efficiency of collecting the generated IR photons was optimized.² By combining these two factors, we were able to enhance the detection sensitivity to such a level that only 15-min observation time is required to cover the entire InSb spectral range (1800–7800 cm^{-1}) with a spectral resolution of 1 cm^{-1} .

An atomic or a molecular transition falls into the IR range if the upper and lower state of the transition are separated by an IR frequency. An electric dipole transition of a homonuclear diatomic molecule takes place from the vibrational-rotational level of an electronic state to another level which belongs to a different electronic state. Since in general the stable diatomic molecules have their first electronic excited state a few electron volts above the ground state, the IR emission of a homonuclear diatomic molecule is produced by an electronic transition which does not involve the ground state. It must take place between two different electronic excited states. The IR atomic emission occurs in a similar situation. It takes place between two excited states which are separated by the IR energy. These two situations for the electronic transitions contrast to the normal IR transition, which is found either in a heteronuclear or in a polyatomic molecule. It involves a vibrational-rotational transition within the same electronic state, usually within the ground electronic state.

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2. Experimental Setup

A central feature of our experimental setup is a 30-m long, 1-m diam cylinder used as a container of the glow discharge source, which is formed between a 12-m long central electrode and the external wall as shown in Fig. 1. An ac 60-Hz voltage of up to 1000 V is applied between the electrodes, activating the discharge. The interferometer accepts the IR radiation through a KBr lens placed at the exit port of the discharge source. The interferogram signal is detected by an InSb detector housed in a liquid nitrogen Dewar. The path difference is monitored by the interference fringe of the He-Ne cw laser line of 6328 Å (air wavelength). The detector output is properly ac amplified, synchronously demodulated, integrated, and finally converted to a digital signal by an analog-to-digital converter, which is triggered by the zero crossing position of the laser interference fringe reference signal. The digitized interferogram signal is then recorded on a mass storage device (a floppy disk) under the control of an LSI/11 minicomputer. After completion of the interferogram measurement, the interferogram data are postprocessed using our central site large-scale computer, CDC CYBER system, for the Fourier transformation etc.

The optical cell which is used to house our glow discharge source is generally known as the Pfund cell.³ The discharge column formed between the electrodes is seen thrice along the optical path, thus forming an equivalent 36-m long discharge column. The discharge region extends only $\frac{1}{3}$ of the entire cell length, leaving $\frac{2}{3}$ of the cell a discharge-free space. This apparent disadvantage created by the discharge-free region is a blessing in disguise from the experimental point of view, since it prevents the mirror contamination caused by the electron bombardment.

An important parameter which controls our glow discharge is the excitation energy released to the atoms and the molecules. A rough estimate of the excitation energy can be obtained in the following way. The electric field in the cell is given as a function of distance r (measured from the center) by

$$E = \frac{V}{r \left(\ln \frac{b}{a} \right)}, \quad (1)$$

where V is the electric potential applied between the electrode of radius a and the wall of radius b . The electrons pick up their energy under the applied electric field and lose it when they collide with a molecule or an atom. The loss of energy occurred as the collision turns into the energy for exciting the collision partners, for our case either molecule or atom. The energy loss suffered at the collision is usually resupplied between collisions. The mean free path $\langle x \rangle$ of the electrons, i.e., the mean distance between the successive collisions, is generally characterized by

$$\langle x \rangle = 1/(n\sigma), \quad (2)$$

where n is the number density of the colliding molecules and σ is a quantity called the collision cross section. If

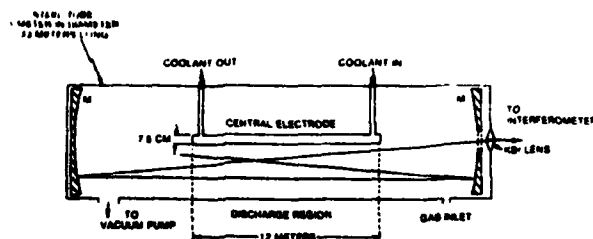


Fig. 1. Schematic representation of the discharge column (not to scale). Mirrors M_1 and M_2 are focused on each other, resulting in three passes through the discharge column.

an electron moves parallel to the field, it gains its energy by $e(x)E$, which is calculated by

$$e = e(x)E = \frac{eVp_0}{r \left(\ln \frac{b}{a} \right) N_0 \sigma} \quad (3)$$

for the gas pressure p . In this expression, N_0 is the number density at the standard pressure p_0 . It is seen that the excitation is the highest in the vicinity of the electrode and that it reduces toward the outer wall. For a typical example, we can assume $\sigma = 10^{-16} \text{ cm}^2$, $V = 1000 \text{ V}$, and $n = N_0 p/p_0 = 7.07 \times 10^{15}$ for $p = 0.2 \text{ Torr}$. The field at $r = 30 \text{ cm}$ is $\sim 13 \text{ V/cm}$, while the mean free path is $\sim 1.4 \text{ cm}$. The energy gain per collision in the area at $r = 30 \text{ cm}$ would reach $18 \text{ eV} = 145,000 \text{ cm}^{-1}$. In reality, the cross section σ varies dependent on the electron energy, and the electrons may lose only a part of their energy by the inelastic collision process. Nonetheless, the value estimated above for the excitation energy agreed well with the experimental data obtained. In the glow discharge of oxygen, for example, observed are many IR atomic oxygen lines which are produced in transition between two highly excited atomic levels. By identifying the levels involved for the observed IR atomic OI lines, we estimated the excitation energy in our glow discharge generally reaching a level of 20 eV. Even though some excitations may exceed the value by a substantial degree, it is safe to assume that a majority of the IR photons observable in our experiment are indeed generated in the processes which require an excitation energy of $\sim 20 \text{ eV}$ or less.

One thing noticed is that the excitation is very sensitive to the gas pressure. Once the gas pressure is above 0.5 Torr, the glow discharge which is indicative of transitions between the electronic states is confined to the vicinity of the electrodes, leaving a dark space elsewhere. For heteronuclear diatomic molecules, the IR emission does not necessitate the electronic transition. An absence of the visible glow discharge does not eliminate a possible IR emission. However, for homonuclear molecules, the visible glow discharge which usually indicates a presence of the electronic transitions to the ground state is necessary to produce IR transition.

The glow discharge is run at 60-Hz ac obtained from the ordinary 60-Hz power through a step-up trans-

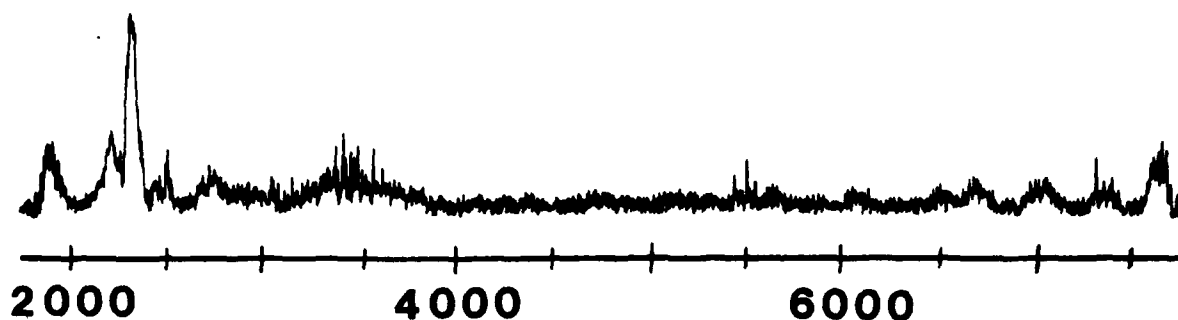


Fig. 2. Glow discharge spectrum of air.

former. Direct current voltages failed to produce a stable glow discharge. The central electrode is usually water-cooled.

The spectrum shown in Fig. 2 is a typical result produced by a glow discharge in 0.1 Torr of air. Identifiable molecular features in the spectrum are NO, N₂, CO, CO₂, N₂O, OH, NH, and NO₂. The atomic features contain O and N. Each spectral feature of these species as well as of others was studied by observing the IR glow discharge emissions formed in various gas samples in addition to those produced in air. Specific mixtures were selected to produce the spectral data necessary for interpreting those features observable in the air discharge.

III. Emission Spectra of Various Atmospheric Species

The spectrum shown in Fig. 2 was taken with a resolution of $\sim 1.0 \text{ cm}^{-1}$. A feature observable between 2000 and 2400 cm^{-1} consists of CO, N₂O, CO₂, and possibly others. The vibrational fundamental ($\Delta v = 1$) of the NO ground state is observable in 1800 cm^{-1} , the lowest frequency range covered by the InSb detector. A feature which appears as a group of lines at 2500 cm^{-1} consists of many atomic lines.⁴ The transition frequency of 2470 cm^{-1} corresponds approximately to the energy difference between $n = 4$ and $n = 5$ orbit of the hydrogenlike atoms. Consequently, all atoms contained in the gas samples would emit IR lines in a confined spectral region centered at 2470 cm^{-1} . We found atomic lines of H, N, O, and He in this region. The features observable between 2500 and 4000 cm^{-1} are of N₂, NH, OH, and NO₂. The features above 5000 cm^{-1} are predominantly those of the N₂ first positive band ($B^1\pi_g - A^3\Sigma_u$).⁵ In addition to these molecular features, various atomic lines of H, O, and N spread over the entire InSb region.

The following description provides a survey of the spectral features produced by various atmospheric species. As mentioned above, the glow discharge formed several molecular products which were not found in the original gas samples. The present paper will not discuss the formation mechanism of these products. All the measurements were done in inte-

grating the emission intensity using the normal lock-in technique. The formation processes of the glow discharge by-product would be better studied by using the time-resolved spectroscopic technique.

A. Atomic Feature

1. Hydrogen

The atomic lines of hydrogen were observed in the glow discharge emission of air whenever the sample was moist. Table I lists the atomic H lines observed in the IR. No molecular transitions of hydrogen were observed in the IR, even though several known excited electronic states of H₂ are spaced by the IR frequencies. The atomic hydrogen may have been easily formed because of a low dissociation energy at the ground state ($X^1\Sigma_g^+$).⁶

The glow discharge emissions were to a great extent affected by admission of hydrogen into the gas sample. There were two notable effects observed in the discharge emission: suppression of the CO vibrational fundamental which would otherwise accompany as a parasitic emission; formation of two hydrides, OH and NH.

2. Oxygen

The atomic lines of oxygen were observed over a wide spectral range. The line position is listed in Table II. It is similar to the hydrogen case where no molecular transitions were observed. The low dissociation energy of the O₂ ground state ($X^3\Sigma_g^-$) contributes to the formation of the atomic oxygen in the glow discharge.⁷ The recent data compiled for the atomic IR lines by

Table I. Observed Atomic Hydrogen Lines (cm^{-1})

n	$\Delta n = 1$	$\Delta n = 2$	$\Delta n = 3$	$\Delta n = 4$
1				
2				
3	5331.55	7799.29		
4	2467.75	3808.25	4616.53	
5		2148.79	2673.39	3033.05
6				

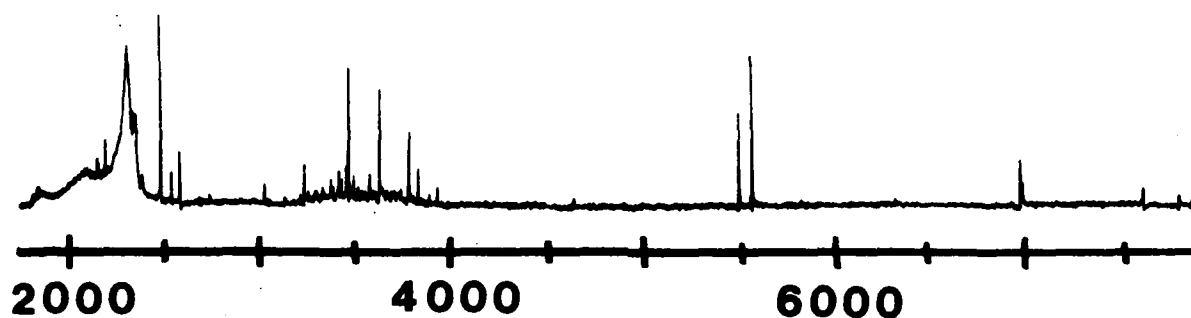


Fig. 3. Glow discharge spectrum of O_2 .

Outred⁴ do not contain the oxygen lines below 3819 cm^{-1} . Figure 3 shows the glow discharge emission spectrum of the oxygen gas.

Figure 4 is a sketch showing the atomic oxygen (OI) energy levels⁸ together with the IR lines observed in our measurement. The energy of these levels is referenced to the ground state of atomic oxygen $(1S)^2(2S)^2(2p)^4\ ^3P_2$, which is located at $\sim 40,000\ cm^{-1}$ above the molecular O_2 ground state $X^3\Sigma_g^-$. As mentioned above, the

estimate made on the electron energy available for the excitation agrees with the excitation energy measured from the observed atomic oxygen lines.

3. Nitrogen

The IR emission from the nitrogen gas contains few atomic nitrogen lines. The data compiled by Outred⁴ contain no NI lines below $5000\ cm^{-1}$. The feature at $2470\ cm^{-1}$ consists of many lines, as listed in Table III, with their transition identification.⁹ Figure 5 shows the atomic NI emission at $2470\ cm^{-1}$.

(cm^{-1})	Transition
7593.7	$4s^3S^0-3p^3P$
6289.5	$5d^3D-4p^3P$
5546.9	$4f^3F-3d^3D$
5479.4	$4f^3F-3d^3D^0$
3918.9	$6f^3F-4d^3D$
3876.2	$6f^3F-4d^3D$
3819.9	$8s^3S-5p^3P$
3819.9	$6g^3G-4f^3F$
3770.7	$4d^3D-4p^3P$
3617.2	$4p^3P-4s^3S$
3455.4	$4p^3P-4s^3S$
3226.9	$3d^3D-4p^3P$
3021.9	$5s^3S-4p^3P$
2731.0	$5s^3S^0-4p^3P$
2575.7	$5f^3F-4d^3D^0$
2532.7	$5f^3F-4d^3D^0$
2477.3	$5g^3G-4f^3F$
2192.1	$4p^3P-3d^3D^0$
2154.6	$7g^3G-5f^3F$
2150.5	$7f^3F-5g^3G$

Table III. Observed Line Position, Observed and Calculated Intensity of NI Transition between $(^3P)5g$ and $(^3P)4f$ Configuration

j	K'	K''	Position (cm^{-1})	Relative intensity	
				Observed	Calculated
0	4	3	2484.9	1.0	1.0
1	3	2	2480.6	0.8	0.7
	4	3	2484.1	1.0	0.9
	5	4	2481.9	1.3	1.2
2	2	1	2500.3	0.5	0.4
	3	2	2479.0	0.6	0.6
	4	3	2489.6	2.7*	0.8
	5	4	2486.7	1.3	1.1
	6	5	2489.3	1.4	1.4

* Blended with He I line.

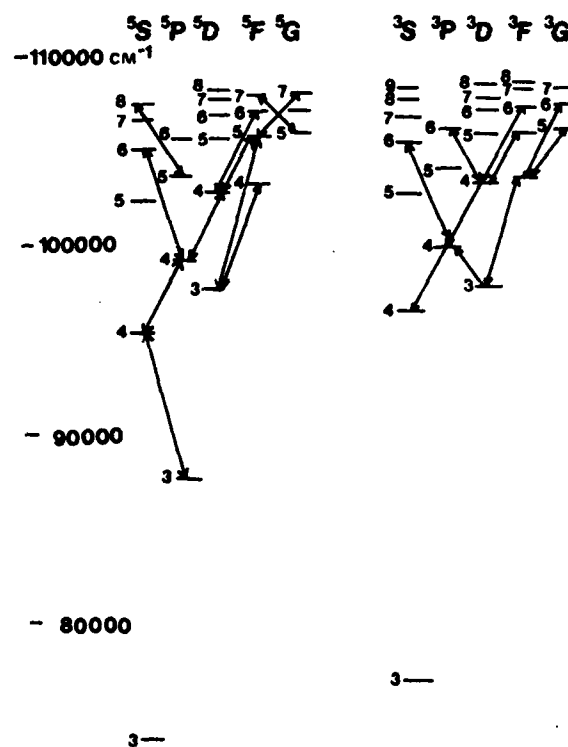


Fig. 4. Energy level diagram of atomic OI indicating observed transitions.

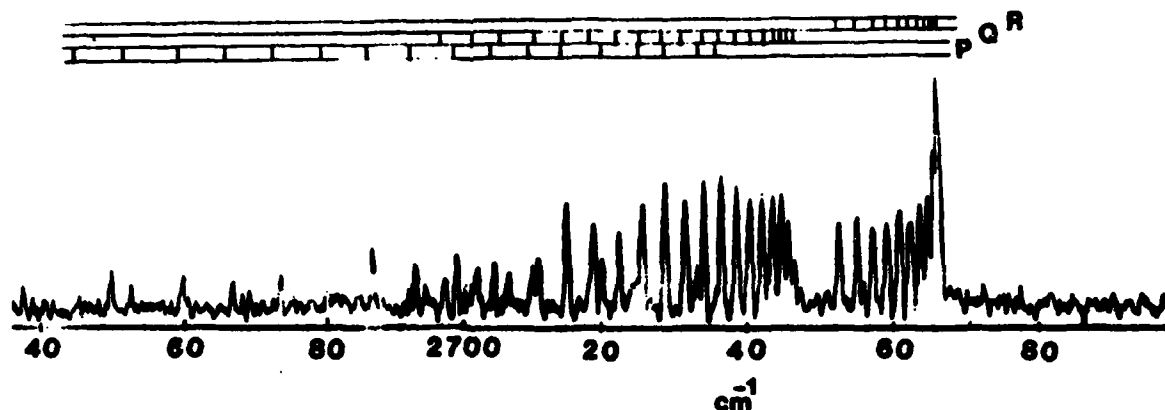


Fig. 7. Spectrum of the $w^1\Delta - a^1\pi$ (0-0) transition.

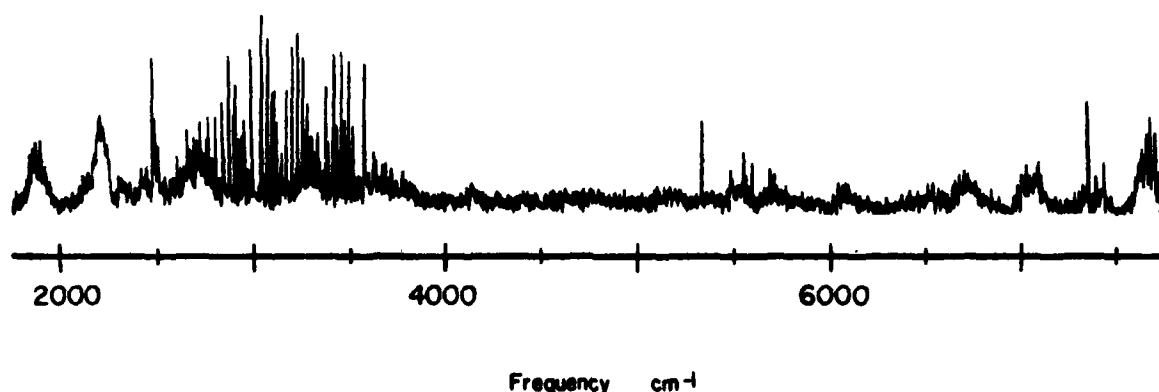


Fig. 8. Glow discharge spectrum of air mixed with H_2 . Mixture ratio: air, 3 and H_2 , 1.

Table IV. Spectroscopic Constants of NH Electronic Ground State ($X^2\Sigma$)

	(cm^{-1})
ω_e	3280.86
$\omega_e x_e$	77.40
$\omega_e y_e$	-0.14
B_e	16.674
α_e	0.650
D_e	17.6×10^{-4}
β	-0.41×10^{-4}
λ_0^a	0.911
λ_1^a	-0.013
γ_0^b	-0.056
γ_1^b	0.0037

^a $\lambda = \lambda_0 + \lambda_1 v$.

^b $\gamma = \gamma_0 + \gamma_1 v$.

condition; its intensity varies over a large range from an undetectably weak level to an extremely strong level. The other two bands which are seen in the low frequency region remained consistently strong. The characteristics of both bands, one at 2740 cm^{-1} and another at 3000 cm^{-1} , remain consistent; a singlet structure was observed for the 2740-cm^{-1} band shown in Fig. 7 and a triplet structure of the 3000-cm^{-1} band. The 2740-cm^{-1} band was identified as the $w^1\Delta_u - a^1\pi_g$

transition. We were able to determine the spectroscopic parameters of this band and found them in good agreement with those determined from the UV spectral data.

2. OH

It was found that enhancement of the hydride emission, OH and NH, accompanied an increase of the moisture in the sample air. The spectrum shown in Fig. 8 is the glow discharge emission formed in the air mixed with hydrogen. Our experiments indicate that these hydrides are formed with the presence of hydrogen, either atomic or molecular. The presence of H_2O does not seem to be required for the formation of the hydrides. The infrared OH band was thoroughly studied by Maillard *et al.*¹³ Our measurement of the OH line position agrees well with them.

3. NH

A unique feature discovered in our study is the vibrational fundamental transition of the NH free radical in its electronic ground state ($^3\Sigma^-$). The NH lines were observed in the discharge formed in air. It was generally considered that the decomposition process, $NH_3 \rightarrow$

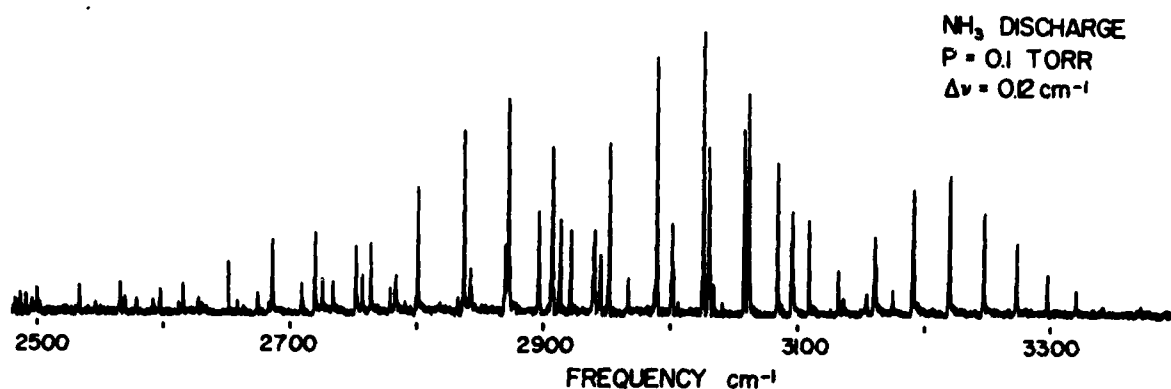


Fig. 9. Infrared spectrum of NH ($^3\Sigma$); spectral resolution 0.12 cm^{-1} .

$\text{NH}_2 \rightarrow \text{NH}$, is the feasible generation mechanism for this free radical. However, the spectra taken with the air/ H_2 mixture showed not only a predicted increase in the OH band but also a striking enlargement in the NH bands. A presence of NH in the glow discharge emission found in the air/ H_2 or N_2/H_2 mixture indicates that the recombination process is undoubtedly responsible for NH formation in these gas samples.

The vibrational-rotational transition of NH exhibits a more complex structure than that of the singlet. The NH spectrum in Fig. 9 was taken with a resolution of 0.1 cm^{-1} , which was adequate for spectral analysis.¹⁴ Table IV lists the spectroscopic constants, which are more accurate than those previously measured using the UV data.¹⁵

4. NO

The NO band was seen in the air discharge shown in Fig. 2. A complementary relation was observed between the intensity of the NO and the NH bands. With introduction of extra hydrogen to the discharge gas, a weakening of the NO band was observed with an enhancement of the NH band.¹⁶

IV. Molecular Emission in the $2000\text{--}2400\text{ cm}^{-1}$ Region

The feature observed between 2000 and 2400 cm^{-1} is composed of several bands, the CO fundamental, the $\text{N}_2\text{O } \Delta\nu_3 = 1$ transition,¹⁷ the $\text{CO}_2 \Delta\nu_3 = 1$ transition, and possibly others. The intensity pattern was found critically influenced by the discharge condition. The most persistent feature is the ν_3 transition of N_2O . The excitation of the CO_2 band is affected by the presence of N_2 . In our glow discharge condition, an exact nature of the correlation between the CO_2 and the N_2 excitation is unclear. A detailed study of the emission in this region requires a spectral resolution better than 0.1 cm^{-1} , which is the limit of our experiment.

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A NEW ROTATION-VIBRATION HAMILTONIAN

L.S. Mayants

Abstract

The conventional, rather tangled rotation-vibration Hamiltonian, whose coefficients are expressed in terms of normal coordinates, is shown to be appropriate only for small enough atomic displacements. A new, exact rotation-vibration Hamiltonian is obtained in an explicit form, whose coefficients can be expressed in terms of Cartesian components of the atomic displacements. The method used for the construction of this Hamiltonian is: (1) calculation of the matrix of derivatives of the set of atomic Cartesian coordinates in the initial rest coordinate system with respect to the set of coordinates describing separately translational, rotational, and internal motions of a molecule; (2) construction of the inverse matrix; (3) calculation of the kinetic part K' of the rotation-vibration Hamiltonian; (4) similarity transformation of K' by making use of the Jacobian of the initial coordinates with respect to the new ones, which cancels the terms linear in momenta canonically conjugate to the internal coordinates; (5) obtaining the final form of the Hamiltonian. The new Hamiltonian allows one to represent it easily in the form of the corresponding differential operator, which opens the door also to the utilization of methods of approximate computation of rotation-vibration spectra other than the perturbation one. It is proven, by the way, that the supposition of the existence of an equilibrium configuration of a molecule is quite enough for constructing the Hamiltonian, Eckart's conditions turning out to be not only approximate, but also unnecessary.

The new rotation-vibration Hamiltonian can prove to be of special importance for computation of molecular spectra in the case of large rotation or vibration quantum numbers, in particular for computation of spectra of molecules near their dissociative limits.

1. Introduction

A rotation-vibration Hamiltonian was introduced for the first time by Wilson and Howard,¹ and modified somewhat later by Darling and Dennison.² Its general form was considerably simplified by Watson.³ Nevertheless, the conventional Hamiltonian still remains rather tangled. The fact that its coefficients are expressed in terms of normal coordinates, the atomic displacements being supposed to be linear combinations of those, makes the Hamiltonian approximate, because in the general case the supposition mentioned cannot hold. Besides, the same fact leads to certain difficulties in the practical utilization of the Hamiltonian, in particular since its coefficients are implicit functions of the force coefficients and should be changed in the process of computation of spectra, if the potential energy is improved.

The methods of the numerical computation of the rotation-vibration spectra based on the conventional Hamiltonian can apparently be only various versions of the perturbation method. These versions usually utilize up to the sixth order approximations of that method.⁴ In the meantime, the resolution of rotation-vibration spectra has been greatly increased due to the development of technique of infrared molecular spectroscopy. And even though the conventional methods of computation proved apparently to work sufficiently good in many cases, they are not accurate enough

for the computation of the spectra in the case of rather large rotation or vibration quantum numbers.

Thus the accuracy of the computation of the rotation-vibration spectra turned out to fall behind the accuracy of the contemporary experimental data. This fact requires increasing the accuracy of the computation of the spectra. But the higher the accuracy required, the higher should be the order of the perturbation method approximation to be employed. And this leads, in turn, to more and more complicated computations. Besides, appearance of even an approximate occasional degeneracy in the energy levels causes the necessity of utilizing some special computational methods. And all the difficulties cannot be overcome when using the conventional Hamiltonian, the more so because this Hamiltonian is not quite accurate by itself.

Under the circumstances, it seems interesting to try to obtain a rotation-vibration Hamiltonian in explicit form and expressed in terms of Cartesian displacements of atoms, which would make it generally valid. The aim of this article is to show how this task was accomplished.

In order to obtain the Hamiltonian needed it was necessary to give up the well known common way of obtaining a Hamiltonian in coordinates other than Cartesian ones, and to try a different method. The method used is the direct representation of the Hamiltonian originally written down in Cartesian coordinates, in the coordinates describing the translational, rotational, and internal motions of a molecule, separately.

In any coordinates, the Hamiltonian has the form

$$H = K + V \quad (1)$$

where K is the kinetic and V is the potential part of the Hamiltonian.

Certainly, only K should be considered, since V does not need any transformation.

In the initial rest coordinate system (laboratory system) the differential operator K has the form

$$K = \frac{1}{2} \sum_{i=1}^n \epsilon_i (p^{(i)}, p^{(i)}). \quad (2)$$

Here

$$p^{(i)} = -i\hbar \nabla_i; \nabla_i = \frac{\partial}{\partial \mathbf{r}^{(i)}} = \left(\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i} \right). \quad (3)$$

$\mathbf{r}^{(i)} = (x_i, y_i, z_i)$ is the radius vector of i th atom; $a_i = r_a^{(i)}$ ($a=x, y, z$) is the a th Cartesian coordinate of i th atom; $\epsilon_i = m_i^{-1}$ is the inverse mass of i th atom; and n is the number of atoms in a molecule.

We choose the new coordinates as follows: $X^0 = R_x^0$, $Y^0 = R_y^0$, and $Z^0 = R_z^0$ are the Cartesian coordinates of the center of mass of the molecule in the initial rest coordinate system; $\phi = \Omega_1$, $\theta = \Omega_2$, and $\chi = \Omega_3$ are Euler's angles determining the spatial orientation of the molecule equilibrium configuration and, hence, the spatial orientation of the rotating coordinate system rigidly attached to it; q_j ($j=1, 2, \dots, N$) are some independent internal coordinates describing a deformation of the molecule relative to its equilibrium configuration, and $N = 3n-6$ is the number of these coordinates.⁵

In the chosen new coordinates, Eq. (3) yields

$$\nabla_i = \sum_a \nabla_i^0 \frac{\partial}{\partial R_a^0} + \sum_j \nabla_i^0 \Omega_j \frac{\partial}{\partial \Omega_j} + \sum_j \nabla_i^0 q_j \frac{\partial}{\partial q_j}. \quad (4)$$

By introducing

$$-i\hbar \frac{\partial}{\partial R_\alpha^0} = P_\alpha^0; \quad -i\hbar \frac{\partial}{\partial \Omega_j} = \pi_j; \quad -i\hbar \frac{\partial}{\partial q_j} = P_j \quad (5)$$

we get from Eqs. (3) and (4)

$$p^{(i)} = \sum_{\alpha} V_i R_\alpha^0 P_\alpha^0 + \sum_j V_i \Omega_j \pi_j + \sum_j V_i q_j P_j. \quad (6)$$

(From now on we will widely use matrix calculus. We will use the same notation $\underline{a} = (a_1, a_2, \dots, a_l)$ for both the vector $\underline{a}$ with components a_j and the column matrix $\underline{a}$ with elements a_j ($j=1, 2, \dots, l$). A row matrix $\underline{b}$ with elements b_j ($j=1, 2, \dots, k$) will be written as $\underline{b} = ||b_1 b_2 \dots b_k||$. $\underline{\hat{C}}$ will denote the matrix transposed to $\underline{C}$. The same notation will apply to block matrices. E_n will denote an n by n unit matrix.)

It only remains now to find all the $V_i R_\alpha^0$, $V_i \Omega_j$, and $V_i q_j$, and to substitute them in Eq. (6), and then to replace the $p^{(i)}$ in Eq. (2) by making use of the results obtained. It is very simple to calculate $V_i R_\alpha^0$. Indeed, by definition

$$\vec{R}^0 = M^{-1} \sum_i m_i \vec{r}^{(i)} \quad (7)$$

where $\vec{R}^0$ is the radius vector of the center of mass of the molecule and $M = \sum_i m_i$ is the total mass of it. Therefore

$$V_i \vec{R}^0 = M^{-1} E_3 m_i \quad (8)$$

where E_3 is a 3 by 3 unit matrix.

But it is not so simple to find $V_i \Omega_j$ ($j=1, 2, 3$) and $V_i q_j$ ($j=1, 2, \dots, N$), because it is impossible to represent ϕ , θ , χ , and all the q_j as explicit functions of the x_i , y_i , and z_i ($i=1, 2, \dots, n$). To find these quantities, we calculate, first, the $3n$ by $3n$ matrix

$$D = \begin{vmatrix} \frac{\partial r^{(1)}}{\partial R^0} & \frac{\partial r^{(1)}}{\partial \Omega} & \frac{\partial r^{(1)}}{\partial q} \end{vmatrix} \quad (9)$$

where

$$\frac{\partial r^{(1)}}{\partial R^0} = \downarrow_{\beta \rightarrow}^{\alpha} \left| \frac{\partial \alpha_1}{\partial R^0_{\beta}} \right| ; \quad \frac{\partial r^{(1)}}{\partial \Omega} = \downarrow_{j \rightarrow}^{\alpha} \left| \frac{\partial \alpha_1}{\partial \Omega_j} \right| ; \quad \frac{\partial r^{(1)}}{\partial q} = \downarrow_{j \rightarrow}^{\alpha} \left| \frac{\partial \alpha_1}{\partial q_j} \right| \quad (10)$$

($\alpha, \beta = x, y, z$). Then we construct the inverse matrix:

$$D^{-1} = \begin{vmatrix} \frac{\partial R^0}{\partial r} \\ \frac{\partial \Omega}{\partial r} \\ \frac{\partial q}{\partial r} \end{vmatrix} = \begin{vmatrix} \frac{\partial R^0}{\partial r^{(1)}} & \dots & \frac{\partial R^0}{\partial r^{(n)}} \\ \frac{\partial \Omega}{\partial r^{(1)}} & \dots & \frac{\partial \Omega}{\partial r^{(n)}} \\ \frac{\partial q}{\partial r^{(1)}} & \dots & \frac{\partial q}{\partial r^{(n)}} \end{vmatrix} \quad (11)$$

from which we can obviously get all the quantities we need, since

$$\frac{\partial R^0}{\partial r^{(1)}} = \downarrow_{\beta \rightarrow}^{\alpha} \left| \frac{\partial R^0_{\alpha}}{\partial \beta_1} \right| ; \quad \frac{\partial \Omega}{\partial r^{(1)}} = \downarrow_{\alpha \rightarrow}^j \left| \frac{\partial \Omega_j}{\partial \alpha_1} \right| ; \quad \frac{\partial q}{\partial r^{(1)}} = \downarrow_{\alpha \rightarrow}^j \left| \frac{\partial q_j}{\partial \alpha_1} \right| \quad (12)$$

The purely analytical calculation of matrix D is given in §2. The construction of matrix D^{-1} , by making use of some important relations concerning the theory of small molecular vibrations, is presented in §§3-5. In §§6-8, the kinetic part, K' , of the rotation-vibration Hamiltonian is constructed in terms of angular and vibrational angular momenta operators. Since K' contains terms linear in P_j , which do not disappear in the zero approximation, an appropriate similarity transformation of that canceling those terms is performed and the final rotation-vibration Hamiltonian is calculated in §§9-10. In the calculation, general formulas for commutators of functions of more than one pair of canonically conjugate operators are used.

2. Calculation of Matrix D

The transformation of any vector $\vec{a}$ given in the rest coordinate system into the corresponding vector $\vec{a}'$ in the rotating coordinate system is of the form⁶

$$\vec{a}' = A_O^{(\Omega)} \vec{a} \quad (13)$$

where $A_O^{(\Omega)}$ is the orthogonal matrix⁷

$$A_O^{(\Omega)} = \begin{vmatrix} \cos\phi\cos\chi - \sin\phi\cos\theta\sin\chi & \sin\phi\cos\chi + \cos\phi\cos\theta\sin\chi & \sin\theta\sin\chi \\ -(\cos\phi\sin\chi + \sin\phi\cos\theta\cos\chi) & -\sin\phi\sin\chi + \cos\phi\cos\theta\cos\chi & \sin\theta\cos\chi \\ \sin\phi\sin\theta & -\cos\phi\sin\theta & \cos\theta \end{vmatrix}. \quad (14)$$

Since $A_O^{(\Omega)-1} = A_O^{(\Omega)}$, the radius vectors $\vec{r}^{(i)}$ and $\vec{r}^{(i)'}$ of i th atom in the rest and rotating coordinate systems, respectively, are related by

$$\vec{r}^{(i)} = \vec{R}_0 + A_O^{(\Omega)} \vec{r}^{(i)'} \quad (15)$$

The $3n$ Cartesian components $\delta a_i (i=1,2,\dots,n; \alpha=x,y,z)$, in the rotating coordinate system, of the atomic displacement vectors

$$\delta \vec{r}^{(i)} = \vec{r}^{(i)} - \vec{R}^{(i)} \quad (16)$$

are generally nonlinear functions of any internal coordinates q_j [$\vec{R}^{(i)}$ is the equilibrium radius vector of i th atom in the rotating coordinate system].

In virtue of Eq. (7), the equation

$$\sum_i \vec{r}^{(i)'} = 0 \quad (17)$$

is valid for any arbitrary $\delta \vec{r}^{(i)}$. At the same time, the well known equation

$$\sum_i (R_\alpha^{(i)} \delta \beta_i - R_\beta^{(i)} \delta \alpha_i) = 0 \quad (\alpha \neq \beta; \alpha, \beta = x, y, z) \quad (18)$$

is valid only for small enough $\delta \vec{r}^{(i)}$. This statement will be proven in Section 4.

From Eq. (15) we get

$$\frac{\partial r^{(1)}}{\partial \lambda^0} = E_3 \quad (19)$$

$$\frac{\partial r^{(1)}}{\partial \lambda} = \left\| \frac{\partial \lambda_o^{(n)}}{\partial \phi} r^{(1)}, \frac{\partial \lambda_o^{(n)}}{\partial \theta} r^{(1)}, \frac{\partial \lambda_o^{(n)}}{\partial \chi} r^{(1)} \right\| \quad (20)$$

$$\frac{\partial r^{(1)}}{\partial \lambda} = \lambda_o^{(n)} \left\| \frac{\partial r^{(1)}}{\partial q_1}, \dots, \frac{\partial r^{(1)}}{\partial q_j}, \dots, \frac{\partial r^{(1)}}{\partial q_N} \right\|. \quad (21)$$

Simple calculations yield

$$\left. \begin{aligned} \frac{\partial \lambda_o^{(n)}}{\partial \phi} &= \lambda_o^{(n)} (-\sigma_x \sin \theta \sin \chi - \sigma_y \sin \theta \cos \chi - \sigma_z \cos \theta) \\ \frac{\partial \lambda_o^{(n)}}{\partial \theta} &= \lambda_o^{(n)} (-\sigma_x \cos \chi + \sigma_y \sin \chi) \\ \frac{\partial \lambda_o^{(n)}}{\partial \chi} &= \lambda_o^{(n)} (-\sigma_z) \end{aligned} \right\} \quad (22)$$

where the matrices

$$\sigma_x = \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{vmatrix}; \sigma_y = \begin{vmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{vmatrix}; \sigma_z = \begin{vmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (23)$$

are closely related to infinitesimal rotations around the axes X' , Y' , and Z' of the rotating coordinate system, respectively.⁸

Eq. (20), in view of Eq. (22), takes on the form

$$\frac{\partial r^{(1)}}{\partial \lambda} = \lambda_o^{(n)} \Lambda_i^{(r)} c^{(n)} \quad (24)$$

where

$$A_i^{(r)'} = - \left\| \begin{matrix} \sigma_x r^{(i)'} \\ \sigma_y r^{(i)'} \\ \sigma_z r^{(i)'} \end{matrix} \right\| = \quad (25)$$

$$= \left\| \begin{matrix} 0 & z_i' & -y_i' \\ -z_i' & 0 & x_i' \\ y_i' & -x_i' & 0 \end{matrix} \right\|$$

and

$$C^{(\Omega)} = \left\| \begin{matrix} -\sin\theta\sin\chi & -\cos\chi & 0 \\ -\sin\theta\cos\chi & \sin\chi & 0 \\ -\cos\theta & 0 & -1 \end{matrix} \right\|. \quad (26)$$

The upper parenthetic index "r" indicates that $A^{(r)'}_i$ is related to rotations; the columns of this matrix being the "modes" of small rotations of the vector $r^{(i)'}_i$ around the respective axes X' , Y' , and Z' of the rotating coordinate system.⁸

In Eq. (21), we can make use of the relation

$$\frac{\partial r^{(i)'}}{\partial q_j} = A_{ij} \quad (27)$$

where A_{ij} is a one by three column matrix whose elements are determined by the choice of internal coordinates, the geometry of the equilibrium configuration of the molecule, and masses of its atoms. We obtain thereby

$$\frac{\partial r^{(i)'}}{\partial q} = \chi_o^{(\Omega)} \left\| \begin{matrix} A_{i1} & A_{i2} & \dots & A_{ij} & \dots & A_{iN} \end{matrix} \right\| \equiv \chi_o^{(\Omega)} A_i. \quad (28)$$

We can rewrite $A_i^{(r)'}$ in Eq. (25), in view of Eq. (16), as

$$A_i^{(r)'} = A_i^{(r)} + \delta A_i^{(r)} \quad (29)$$

where

$$A_i^{(r)} = - \left| \begin{array}{c} \sigma_x R^{(i)} \\ \sigma_y R^{(i)} \\ \sigma_z R^{(i)} \end{array} \right| =$$

$$= \left| \begin{array}{ccc} 0 & R_z^{(i)} & -R_y^{(i)} \\ -R_z^{(i)} & 0 & R_x^{(i)} \\ R_y^{(i)} & -R_x^{(i)} & 0 \end{array} \right| \quad (30)$$

and

$$\delta A^{(r)} = - \left| \begin{array}{c} \sigma_x \delta r^{(i)} \\ \sigma_y \delta r^{(i)} \\ \sigma_z \delta r^{(i)} \end{array} \right| =$$

$$= \left| \begin{array}{ccc} 0 & \delta z_i & -\delta y_i \\ -\delta z_i & 0 & \delta x_i \\ \delta y_i & -\delta x_i & 0 \end{array} \right|. \quad (31)$$

The columns of the composite matrix

$$A^{(r)} = \frac{1}{\downarrow} \left| A_i^{(r)} \right| = (A_1^{(r)}, \dots, A_i^{(r)}, \dots, A_n^{(r)}) \quad (32)$$

represent the modes of small rotations of the equilibrium configuration of the molecule around the respective axes in the rotating coordinate system.⁹

We will also utilize the composite matrix

$$A = \frac{1}{\downarrow} \left| A_i \right| = (A_1, \dots, A_i, \dots, A_n). \quad (33)$$

We can now rewrite matrix D as given in Eq. (9) in the form

$$D = \left| \begin{array}{c} E_3' \\ \chi^{(\Omega)} A^{(r)} C^{(\Omega)} \end{array} \right| \chi^{(\Omega)} A \quad (34)$$

Here

$$E_3' = (E_3, \dots, E_3, \dots, E_3). \quad (35)$$

$\chi^{(\Omega)}$ is the $3n$ by $3n$ diagonal matrix of the form

$$\chi^{(\Omega)} = \left\| \chi_o^{(\Omega)} \delta_{ij} \right\| \quad (36)$$

and $A^{(r)'}$ is obtained from $A^{(r)}$ by substitution of $r^{(1)'}$ for $R^{(1)}$; thus, in view of Eq. (29),

$$A^{(r)'} = A^{(r)} + \delta A^{(r)} \quad (37)$$

where $\delta A^{(r)}$ is composed of $\delta A_i^{(r)}$ in the same way as $A^{(r)}$ of $A_i^{(r)}$.

Let us note, by the way, that the columns of the matrix E' represent the modes of the translations of the molecules as a single whole in the initial rest coordinate system.

3. Construction of the Matrix D^{-1}

To construct the matrix D^{-1} as given in Eq. (11), we will make use of the obvious relation

$$D^{-1}D = E_{3n}. \quad (38)$$

The submatrices of D^{-1} should obviously obey the equations

$$\chi_{R^0}^{\circ} E_3' = E_3 \quad (39a)$$

$$\chi_{\Omega A}^{\chi^{(\Omega)}} A^{(r)'} C^{(\Omega)} = E_3 \quad (39b)$$

$$\chi_{qA}^{\chi^{(\Omega)}} A = E_N \quad (39c)$$

$$\chi_{R^0}^{\circ} \chi_{A}^{(\Omega)} A^{(r)'} C^{(\Omega)} = 0 \quad (39d)$$

$$\chi_{R^0}^{\circ} \chi_{A}^{(\Omega)} A = 0 \quad (39e)$$

$$\chi_{\Omega E_3}^{\circ} = 0 \quad (39f)$$

$$\chi_{\Omega A}^{\chi^{(\Omega)}} A = 0 \quad (39g)$$

$$\chi_{qE_3}^{\circ} = 0 \quad (39h)$$

$$\chi_{qA}^{\chi^{(\Omega)}} A^{(r)'} C^{(\Omega)} = 0 \quad (39i)$$

From Eq. (8) we immediately obtain

$$\hat{V}_R^0 = M^{-1} E_3^m \quad (40)$$

where

$$m = \left\| m_i \delta_{ij} \right\| \quad (41)$$

and it remains only to find $\hat{V}_R$ and $\hat{V}_Q$. In order to perform this task, we will use some relations concerning the theory of small molecular vibrations.

4. Some Necessary Relations

Let $\delta r = (\delta r^{(1)}, \dots, \delta r^{(i)}, \dots, \delta r^{(n)})$ be the column matrix representing the totality of infinitesimal changes in Cartesian coordinates of an n atomic molecule in the initial rest coordinate system; $\delta r^{(i)} = (\delta x_i, \delta y_i, \delta z_i)$ being the one by three column matrix related to i th atom. Let, further, $q^{(c)} = (q^{(t)}, q^{(r)}, q)$ be the column matrix representing the complete set of coordinates describing separately translations, $q^{(t)}$, rotations, $q^{(r)}$, and internal motions, q , of the molecule. Then the relation of δr to $q^{(c)}$ can be represented in the two following forms

$$\delta r = A^{(c)} q^{(c)} \quad (42)$$

$$q^{(c)} = B^{(c)} \delta r, \quad (43)$$

the condition

$$B^{(c)} A^{(c)} = E_{3n} \quad (44)$$

having to be satisfied. In accordance with the form of $q^{(c)}$, we rewrite $A^{(c)}$ and $B^{(c)}$ as

$$A^{(c)} = \left\| A^{(t)} \begin{matrix} \vdots \\ A^{(r)} \end{matrix} \begin{matrix} \vdots \\ A \end{matrix} \right\| \quad (45)$$

$$B^{(c)} = (B^{(t)}, B^{(r)}, B). \quad (46)$$

Equations (42) and (43), in view of Eqs. (45) and (46), respectively, yield

$$\delta r = A^{(t)}_q(t) + A^{(r)}_q(r) + Aq \quad (47)$$

and

$$q^{(t)} = B^{(t)} \delta r \quad (48a)$$

$$q^{(r)} = B^{(r)} \delta r \quad (48b)$$

$$q = B \delta r. \quad (48c)$$

It follows from Eq. (44) that

$$B^{(t)} A^{(t)} = E_3 \quad (49a)$$

$$B^{(r)} A^{(r)} = E_3 \quad (49b)$$

$$BA = E_N \quad (49c)$$

$$B^{(t)} A^{(r)} = 0 \quad (49d)$$

$$B^{(t)} A = 0 \quad (49e)$$

$$B^{(r)} A^{(t)} = 0 \quad (49f)$$

$$B^{(r)} A = 0 \quad (49g)$$

$$BA^{(t)} = 0 \quad (49h)$$

$$BA^{(r)} = 0 \quad (49i)$$

From Eq. (47) we get

$$\frac{\partial \delta r}{\partial q^{(t)}} = A^{(t)}; \quad \frac{\partial \delta r}{\partial q^{(r)}} = A^{(r)}; \quad \frac{\partial \delta r}{\partial q} = A. \quad (50)$$

By comparing this with Eqs. (19), (24), and (28), respectively, we find, in view of the fact that for the case under consideration $\lambda_o^{(\Omega)} = E_3$,

$$A^{(t)} = E'_3 \quad (51)$$

while matrices $A^{(r)}$ and A are those given in Eqs. (32) and (33), respectively.

The matrix B is the well known matrix used in calculations of molecular vibrations. Its elements can be easily found and depend only on the choice of internal coordinates and the geometry of the molecule.¹⁰⁻¹² To find of

what a form are matrices $B^{(t)}$ and $B^{(r)}$, we will make use of the equation

$$T^{(c)} = \lambda^{(c)} m \lambda^{(c)} \quad (52)$$

which connects the kinetic energy matrix m [see Eq. (41)] in the δr coordinates with the total kinetic energy matrix $T^{(c)}$ in the $q^{(c)}$ coordinates. In the case under consideration, translations, rotations, and internal motions of a molecule are fully separated, and we can represent $T^{(c)}$, in accordance with the form of $q^{(c)}$, as

$$T^{(c)} = \begin{vmatrix} T^{(t)} & 0 & 0 \\ 0 & T^{(r)} & 0 \\ 0 & 0 & T \end{vmatrix} \quad (53)$$

where $T^{(t)}$, $T^{(r)}$, and T are the kinetic energy matrices for the translations, rotations, and internal motions, respectively.

From Eq. (52) we get, in view of Eq. (44),

$$B^{(c)} = T^{(c)} - \lambda^{(c)} m \lambda^{(c)}. \quad (54)$$

Equation (54) yields, in view of Eqs. (45) and (46),

$$B^{(t)} = G^{(t)} \lambda^{(t)} m \quad (55a)$$

$$B^{(r)} = G^{(r)} \lambda^{(r)} m \quad (55b)$$

$$B = \begin{vmatrix} B_1 & \dots & B_1 & \dots & B_n \end{vmatrix} = G \lambda m \quad (55c)$$

where

$$G^{(t)} = T^{(t)-1}; \quad G^{(r)} = T^{(r)-1}; \quad G = T^{-1}. \quad (56)$$

Comparing Eqs. (52) and (53), we find, in view of Eq. (51), and Eqs. (32) and (30), respectively,

$$T^{(t)} = \sum_i m_i E_i = \sum_i m_i E_3 = M E_3 \quad (57)$$

and

$$T(r) = \lambda(r)_{mA(r)} = \sum_i \lambda_i(r) A_i(r) \equiv I =$$

$$= \begin{vmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & I_{zz} \end{vmatrix} \quad (58)$$

where

$$I_{\alpha\alpha} = I_{\beta} + I_{\gamma} \quad (\alpha \neq \beta \neq \gamma); \quad I_{\alpha} = \sum_i R_{\alpha}^{(i)2}; \quad I_{\alpha\beta} = \sum_i R_{\alpha}^{(i)} R_{\beta}^{(i)} \quad (\alpha \neq \beta). \quad (58a)$$

Hence

$$G(t) = M^{-1} E_3 \quad (59a)$$

$$G(r) = I^{-1} \quad (59b)$$

(I is known to be the moment of inertia matrix. G is the well known matrix used in calculations of molecular vibrations, whose elements for a number of internal coordinates are tabulated in some works.¹⁰⁻¹²)

Thus we finally find

$$B(t) = M^{-1} E_{3m} \quad (60a)$$

$$B(r) = I^{-1} \lambda(r)_m \quad (60b)$$

We will also need the equation¹³

$$A = \epsilon B^T \quad (61)$$

following immediately from Eq. (55c), where

$$\epsilon = m^{-1} = ||\epsilon_{ij}|| \quad (62)$$

and the equation

$$B \epsilon B^T = G = ||g_{ij}|| \quad (63)$$

which results from Eqs. (61) and (49c).

We can now easily see that Eq. (49f) is a corollary of Eq. (49d), and Eq. (49h) is that of Eq. (49e); both pairs of equations reflecting the law of conservation of the center of mass of the molecule. Eq. (49i) is the corollary of Eq. (49g) and both can be rewritten, in view of Eqs. (32) and (30), as a set of equations

$$\sum_i (b_{j\alpha}^{(i)} R_{\beta}^{(i)} - b_{j\beta}^{(i)} R_{\alpha}^{(i)}) = 0 \quad (\alpha, \beta = x, y, z) \quad (64a)$$

or

$$\sum_i (R_{\alpha}^{(i)} a_{j\beta}^{(i)} - R_{\beta}^{(i)} a_{j\alpha}^{(i)}) = 0 \quad (\alpha, \beta = x, y, z) \quad (64b)$$

where $b_{j\alpha}^{(i)}$ is an element of the matrix B and $a_{j\alpha}^{(i)}$ is the corresponding element of the matrix A; the upper parenthetic index i numbering the atoms, the lower index j numbering the internal coordinates, and the index α referring to the α th Cartesian coordinate of an atom.

Equation (18) results from Eq. (64b), provided Eq. (47) is valid. But Eq. (47) cannot generally hold for any $\delta r^{(i)}$ —it should be valid, generally speaking, only for small enough $\delta r^{(i)}$ that can be represented as linear functions of any internal coordinates q_j . And it is precisely this fact which proves the statement following after Eq. (18).

Equation (64) should, in turn, be valid for any arbitrary choice of internal coordinates q_j , which is possible only because the matrices B and B', respectively, A and A' for the corresponding different sets of coordinates q and q' are related by a linear transformation. Hence, the fulfillment of Eq. (64a) for all the matrices B follows from their fulfillment for any of them. Matrix B has the simplest form when small changes in the distances between pairs of atoms are chosen as internal coordinates. In

this case the internal coordinates q_{ii} , corresponding to the pair of i th and i' th atoms has nothing to do with all the other atoms, and, therefore, all the elements of the respective row of matrix B are zeros, except for those referring to i th and i' th atoms, which are¹⁴ (up to a sign) $(R_{\alpha}^{(i)} - R_{\alpha}^{(i')})l_{ii}^{-1}$ and $(R_{\alpha}^{(i')} - R_{\alpha}^{(i)})l_{ii}^{-1}$, respectively, where l_{ii} is the equilibrium distance between i th and i' th atoms. Substituting this in Eq. (64a), we get identically

$$(R_{\alpha}^{(i)} - R_{\alpha}^{(i')})R_{\beta}^{(i)} - (R_{\beta}^{(i)} - R_{\beta}^{(i')})R_{\alpha}^{(i)} + (R_{\alpha}^{(i')} - R_{\alpha}^{(i)})R_{\beta}^{(i')} - (R_{\beta}^{(i')} - R_{\beta}^{(i)})R_{\alpha}^{(i')} = 0 \quad (65)$$

Thus, Eq. (64b) for any choice of internal coordinates follows directly from the identity represented by Eq. (65). But this means that, in distinction to Eqs. (49d) and (49e), Eq. (49g) does not reflect any physical law. On the contrary, Eq. (18), which can be interpreted as the equality of the angular momentum corresponding to small deformations of a molecule to zero, results in the last analysis from the mathematical identity (65). And this fact eliminates all the difficulties related to the problem of choosing the rotating coordinate system.¹⁵

5. Construction of Matrix D^{-1} (continued)

It is obvious that $\hat{V}R^0$ as given in Eq. (40) coincides with $B^{(t)}$ as given in Eq. (60a). Therefore, Eqs. (39a), (39d), and (39e), in view of Eqs. (49a), (49d), and (49e), are satisfied (the commutativity of $\hat{V}R^0$ with $\hat{\chi}^{(\Omega)}$ is to be taken into consideration). In order that matrix $\hat{V}\Omega$ satisfy Eqs. (39f) and (39g) it should, in view of Eqs. (51), (49f), (49g), and (60b), have the form

$$\hat{V}\Omega = C' \hat{\chi}^{(r)}_{MA}(\Omega) \quad (66)$$

where C' is a 3 by 3 matrix determined by the condition

$$C' \lambda^{(r)}_{MA} (r)' C^{(\Omega)} = E_3 \quad (67)$$

which follows from Eq. (39b). Simple calculations give

$$\lambda^{(r)}_{MA} (r)' \equiv I' = \begin{vmatrix} I'_{xx} & -I'_{yx} & -I'_{zx} \\ -I'_{xy} & I'_{yy} & -I'_{zy} \\ -I'_{xz} & -I'_{yz} & I'_{zz} \end{vmatrix} \quad (68)$$

where

$$I'_{\alpha\alpha} = \sum_i (R^{(i)}_{\beta} \beta_i' + R^{(i)}_{\gamma} \gamma_i'); \quad I'_{\alpha\beta} = \sum_i R^{(i)}_{\alpha} \beta_i' \quad (\alpha \neq \beta) \quad (69)$$

(α, β, γ is any of x, y, z). Therefore

$$C' = C^{(\Omega)'} G^{(r)'} \quad (70)$$

where

$$C^{(\Omega)'} = C^{(\Omega)-1} = \begin{vmatrix} -\frac{\sin \chi}{\sin \theta} & -\frac{\cos \chi}{\sin \theta} & 0 \\ -\cos \chi & \sin \chi & 0 \\ \sin \chi \operatorname{ctg} \theta & \cos \chi \operatorname{ctg} \theta & -1 \end{vmatrix} \quad (71a)$$

$$G^{(r)'} = \left\| \xi^{(r)'}_{\alpha\beta} \right\| = I'^{-1} \quad (71b)$$

and $\hat{V}_\Omega$ takes on the final form

$$\hat{V}_\Omega = C^{(\Omega)'} G^{(r)'} \lambda^{(r)}_{MA} (\Omega). \quad (72)$$

If we choose $\hat{V}_Q = BA^{(\Omega)}$, then Eqs. (39c) and (39h) would be satisfied, because of Eqs. (49c) and (49h). But Eq. (39i) will not be fulfilled, since, in view of Eqs. (37) and (49i),

$$BA^{(r)'} C^{(\Omega)'} = B \lambda^{(r)}_{MA} C^{(\Omega)'} \neq 0. \quad (73)$$

In order not to disturb the fulfillment of Eqs. (39c) and (39h), and to ensure the satisfiability of Eq. (39i), we should choose $\tilde{V}_q$ in the form

$$\tilde{V}_q = (B - \kappa G^{(r)})' \chi^{(r)}_{mA}(\Omega) \quad (74)$$

where

$$\kappa = (\kappa_1, \dots, \kappa_j, \dots, \kappa_N) = ||\kappa_{ja}|| \quad (75)$$

is an N by 3 matrix determined by the obvious conditions

$$BA^{(r)'} = \kappa G^{(r)'} \chi^{(r)}_{mA}(\Omega) \quad (76)$$

This gives for κ , in view of Eqs. (68) and (71b),

$$\kappa = BA^{(r)'} = B\delta A^{(r)}. \quad (77)$$

Hence, the final expression for $\tilde{V}_q$ is as given in Eq. (74).

6. Construction of the Operator K in the New Coordinates

From Eqs. (40), (72), and (74) we get, respectively,

$$v_1 \tilde{K}^0 = M^{-1} m_1 E_3 \quad (78)$$

$$v_1 \tilde{\chi} = \chi^{(\Omega)}_{m_1 A_1} (r) \chi^{(r)'} \chi^{(\Omega)'} \quad (79)$$

$$v_1 \tilde{q} = \chi^{(\Omega)}_{B_1} - \chi^{(\Omega)}_{m_1 A_1} (r) \chi^{(r)'} \chi^{(\Omega)'} \quad (80)$$

This gives, in view of Eq. (6),

$$p^{(1)} = M^{-1} m_1 P^0 + \chi^{(\Omega)}_{m_1 A_1} (r) \chi^{(r)'} (\chi^{(\Omega)'} \Pi - \tilde{\chi} P) + \chi^{(\Omega)}_{B_1} P \quad (81)$$

where

$$P^0 = (P^0_x, P^0_y, P^0_z); \Pi = (\Pi_\phi, \Pi_\theta, \Pi_\chi); P = (P_1, \dots, P_j, \dots, P_N). \quad (82)$$

Upon introducing Eq. (81) into Eq. (2), we will generally get terms both quadratic and linear in P^0 , Π , and P . In calculation we will use the matrix representation of the scalar product of vectors, namely,

$$(a, b) = \tilde{a} b. \quad (83)$$

It is easy to see now that no terms linear in any P_α^0 , Π_j , or P_j can be due to the term $M^{-1}m_1P^0$ in $p^{(i)}$, because all the terms in $p^{(i)}$ are independent of R^0 . On the other hand, the only nonvanishing quadratic term originating from $M^{-1}m_1P^0$ is, in view of Eq. (40),

$$K^0 = \frac{1}{2} \sum_i \epsilon_{i1} \gamma_i R^0 \gamma_i R^0 P^0 = \frac{1}{2} M^{-1} (P_x^2 + P_y^2 + P_z^2) \quad (84)$$

which is of no interest, since it refers to translations [other quadratic terms containing P^0 vanish due to Eqs. (39f) and (39h)]. Thus we should deal only with

$$K' = K - K^0 = \frac{1}{2} \sum_i \epsilon_{i1} (p^{(i)'} \cdot p^{(i)'}) \quad (85)$$

where

$$p^{(i)'} = \gamma_i \dot{q}_i + \gamma_i \dot{q}_P. \quad (86)$$

7. Introduction of the Angular Momentum and "Vibrational Angular Momentum" Operators

We will, first, consider the operators for the angular momentum components. The operator M_α for α th component of that in a rest coordinate system has the well known form

$$M_\alpha = \sum_i (\beta_i p_\gamma^{(i)} - \gamma_i p_\beta^{(i)}) \quad (87)$$

(α , β , and γ take on any of the values x , y , or z in the indicated succession). By making use of the matrices σ_α as given in Eq. (23), we can rewrite Eq. (87) as

$$M_\alpha = \sum_i \gamma_i^{(i)} \sigma_\alpha p^{(i)}. \quad (88)$$

For the components of the angular momentum along the axes of the rotating coordinate system, we should substitute in Eq. (88) $\gamma_i^{(i)'}$ for $\gamma_i^{(i)}$, and

$A_{\alpha}^{(\Omega)} p^{(1)}$ for $p^{(1)}$, thus obtaining

$$M_{\alpha}^{\prime} = \sum_i \gamma_i^{(1)\prime} \sigma_{\alpha} A_{\alpha}^{(\Omega)} p^{(1)}. \quad (89)$$

Since $\gamma_i^{(1)\prime} \sigma_{\alpha}$, in view of Eq. (25), is ath row of matrix $\lambda_i^{(r)\prime}$, we get from Eq. (89)

$$M = \sum_i \lambda_i^{(r)\prime} A_{\alpha}^{(\Omega)} p^{(1)}. \quad (90)$$

This gives, because of Eqs. (39i), (81), and (68),

$$M = \lambda^{(r)\prime} m A^{(r)} \gamma^{(r)\prime} \gamma^{(\Omega)\prime} \Pi = \gamma^{(\Omega)\prime} \Pi. \quad (91)$$

Besides, we can introduce, in view of Eqs. (55c) and (77),

$$\mu = \lambda^{(r)\prime} \gamma_{BP} = \lambda^{(r)\prime} m A G P = \gamma_{BP}. \quad (92)$$

By comparing this with Eq. (91), we see that μ has the meaning of the operator of the angular momentum corresponding to the internal motions of a molecule, and it is known to be called the operator of the "vibrational angular momentum."

Equations (91) and (92) allow us to rewrite Eq. (86) as

$$p^{(1)\prime} = A_{\alpha}^{(\Omega)} m_1 A_1^{(r)} \gamma_G^{(r)\prime} (M - \mu) + A_{\alpha}^{(\Omega)} \gamma_{B_1 P} \quad (93)$$

and

$$p^{\prime} = A^{(\Omega)} m A^{(r)} \gamma_G^{(r)\prime} (M - \mu) + A^{(\Omega)} \gamma_{BP}. \quad (93a)$$

8. Calculation of the Operator K'

When calculating the RHS of Eq. (85) we get terms both quadratic and linear in $M - \mu$ and P . The former ones are obtained from $\tilde{p}' \epsilon p'$, yielding, in view of Eqs. (93a), (49i), (58), and (63),

$$\frac{1}{2} \tilde{p}' \epsilon p' = \frac{1}{2} \sum_{\alpha, \beta} \gamma_{\alpha \beta} (M_{\alpha} - \mu_{\alpha}) (M_{\beta} - \mu_{\beta}) + \frac{1}{2} \sum_{j, l} g_{jl} P_j P_l \quad (94)$$

where $\gamma_{\alpha \beta}$ are the elements of the matrix

$$r = G^{(r)'} \lambda^{(r)'}. \quad (95)$$

To get the terms of K' linear in $M-\mu$ and P it is convenient to keep the form of $p^{(i)'} in Eq. (85) at right from comma as given in Eq. (93), and at left from comma to use$

$$p^{(i)'} = -i\hbar \left(\sum_j \nabla_1 \lambda_j \frac{\partial}{\partial \lambda_j} + \sum_j \nabla_1 q_j \frac{\partial}{\partial q_j} \right). \quad (96)$$

Thereby we obtain for the linear terms, in view of Eqs. (72), (74), (58), (77), and (49i),

$$\begin{aligned} & -\frac{i\hbar}{2} \left(\sum_{ji} C_j^{(\Omega)'} G^{(r)'} A_1^{(r)} A_0^{(\Omega)} \frac{\partial \lambda_0^{(\Omega)}}{\partial \lambda_j} \{ m_1 A_1^{(r)} \lambda^{(r)'} (M-\mu) + \tilde{B}_1 P \} \right. \\ & \quad \left. - \sum_j \kappa_j G^{(r)'} \lambda \frac{\partial \lambda^{(r)'}}{\partial q_j} (M-\mu) \right) \\ & = -\frac{i\hbar}{2} \sum_a (S'_a + S''_a) (M-\mu) - \frac{i\hbar}{2} \sum_j \epsilon_j P_j \end{aligned} \quad (97)$$

where $C_j^{(\Omega)'}$ is j th row of $C^{(\Omega)'}$.

For any column matrix $f_1 = (f_{1x}, f_{1y}, f_{1z})$ we get, in view of Eqs. (22), (24), and (72),

$$\begin{aligned} \sum_{ji} C_j^{(\Omega)'} G^{(r)'} \lambda_1^{(r)} A_0^{(\Omega)} \frac{\partial \lambda_0^{(\Omega)}}{\partial \lambda_j} f_1 &= \sum_i Sp C^{(\Omega)'} G^{(r)'} \lambda_1^{(r)} A_1^{(r)} A_1^{(f)'} C_i^{(\Omega)} \\ &= Sp G^{(r)'} \sum_i \lambda_1^{(r)} A_1^{(r)'} \end{aligned} \quad (98)$$

where $A_{1(f)}^{(r)'}$ is obtained from $A_1^{(r)'}$ as given in Eq. (25) by substitution $f_{1\beta}$ for $s_{1\beta}$.

For s_a we should write

$$f_1 = m_1 A_1^{(r)} \lambda_a^{(r)'} \quad (99)$$

where

$$G_a^{(r)'} = (g_{xa}^{(r)'}, g_{ya}^{(r)'}, g_{za}^{(r)'}) \quad (100)$$

is ath column of $G^{(r)'}$. Eqs. (30) and (100) yield

$$f_i = (f_{ix}, f_{iy}, f_{iz})$$

$$= m_i (R_z^{(i)} g_{ya}^{(r)'} - R_y^{(i)} g_{za}^{(r)'}, R_x^{(i)} g_{za}^{(r)'} - R_z^{(i)} g_{xa}^{(r)'}, R_y^{(i)} g_{xa}^{(r)'} - R_x^{(i)} g_{ya}^{(r)'}). \quad (101)$$

Furthermore,

$$\sum_i A_i^{(r)} A_i^{(r)'} = \begin{vmatrix} I_{xx}^{(f)} & -I_{yx}^{(f)} & -I_{zx}^{(f)} \\ -I_{xy}^{(f)} & I_{yy}^{(f)} & -I_{zy}^{(f)} \\ -I_{xz}^{(f)} & -I_{yz}^{(f)} & I_{zz}^{(f)} \end{vmatrix} \equiv I^{(f)} \quad (102)$$

where

$$I_{\alpha\alpha}^{(f)} = \sum_i (R_\beta^{(i)} f_{i\beta} + R_\gamma^{(i)} f_{i\gamma}); \quad I_{\alpha\beta}^{(f)} = \sum_i R_\alpha^{(i)} f_{i\beta}. \quad (103)$$

In what follows we will choose the principal inertia axes as the axes of the rotating coordinate system, thus obtaining

$$I^{(f)} = \begin{vmatrix} 0 & I_y g_{za}^{(r)'} & -I_z g_{ya}^{(r)'} \\ -I_x g_{za}^{(r)'} & 0 & I_z g_{xa}^{(r)'} \\ I_x g_{ya}^{(r)'} & -I_y g_{xa}^{(r)'} & 0 \end{vmatrix} \quad (104)$$

where I_α are those given in Eq. (58a). We now finally get from Eqs. (99) and (104)

$$s_\alpha' = \text{Sp} G^{(r)'} I^{(f)} \quad (105)$$

$$= I_\beta (g_{ya}^{(r)'} g_{\alpha\beta}^{(r)'} - g_{y\beta}^{(r)'} g_{\alpha a}^{(r)'}) - I_\gamma (g_{\alpha\gamma}^{(r)'} g_{\beta a}^{(r)'} - g_{\beta\gamma}^{(r)'} g_{\alpha a}^{(r)'}). \quad (\alpha \neq \beta \neq \gamma)$$

For small enough $\delta r^{(i)}$, when $G^{(r)}$ is a symmetric matrix, s'_α obviously takes on the form

$$s'_\alpha = (g_{\alpha\beta}^{(r)}, g_{\alpha\gamma}^{(r)}, -g_{\alpha\alpha}^{(r)}, g_{\beta\gamma}^{(r)}) (I_\beta - I_\gamma). \quad (106)$$

For s_j we have

$$r_i = (b_{jx}^{(i)}, b_{jy}^{(i)}, b_{jz}^{(i)}) \quad (107)$$

which leads, with due allowance for Eq. (55c), to

$$A_{i(f)}^{(r)} = \begin{vmatrix} 0 & b_{jz}^{(i)} & -b_{jy}^{(i)} \\ -b_{jz}^{(i)} & 0 & b_{jx}^{(i)} \\ b_{jy}^{(i)} & -b_{jx}^{(i)} & 0 \end{vmatrix} = \sum_{l=1}^N g_{jl} A_{i(l)}^{(r)} \quad (108)$$

where

$$A_{i(l)}^{(r)} = \begin{vmatrix} 0 & a_{lz}^{(i)} & -a_{ly}^{(i)} \\ -a_{lz}^{(i)} & 0 & a_{lx}^{(i)} \\ a_{ly}^{(i)} & -a_{lx}^{(i)} & 0 \end{vmatrix}. \quad (109)$$

Therefore, in the case under consideration,

$$\sum_i \lambda_i^{(r)} A_{i(f)}^{(r)} = \sum_{l=1}^N g_{jl} \sum_i \lambda_i^{(r)} A_{i(l)}^{(r)}. \quad (110)$$

But, in view of Eq. (68), the RHS of Eq. (110) can be rewritten as

$$\sum_l g_{jl} I'_l \quad (111)$$

where

$$I'_l = \frac{\partial I}{\partial q_l}. \quad (112)$$

Hence, we finally obtain

$$s_j = \text{Sp} G^{(r)}, \sum_{l=1}^N g_{jl} I_{(l)} = \sum_{l=1}^N g_{jl} c_l \quad (113)$$

where

$$c_l = \text{Sp} G^{(r)}, I_{(l)}. \quad (113a)$$

At last, as follows from Eq. (97)

$$s''_{\alpha} = -\sum_j \kappa_j G^{(r)}, I \frac{\partial G^{(r)},}{\partial q_j} = -\text{Sp} \kappa G^{(r)}, I \frac{\partial G^{(r)},}{\partial \tilde{q}}. \quad (114)$$

But

$$\frac{\partial G^{(r)},}{\partial q_j} = -G^{(r)}, \frac{\partial \tilde{I}}{\partial q_j} G^{(r)},. \quad (115)$$

Therefore, in view of Eq. (112),

$$\frac{\partial G^{(r)},}{\partial \tilde{q}} = -G^{(r)}, \tilde{I}'_{\alpha(q)} \quad (116)$$

where

$$\tilde{I}'_{\alpha(q)} = \left\| \tilde{I}'_{(1)} G^{(r)},_{\alpha} \tilde{I}'_{(j)} G^{(r)},_{\alpha} \dots \tilde{I}'_{(N)} G^{(r)},_{\alpha} \right\|, \quad (117)$$

and Eq. (114) with due allowance for Eq. (95) takes on the form

$$s''_{\alpha} = \text{Sp} \kappa \tilde{I}'_{\alpha(q)}. \quad (118)$$

Combining all the results obtained, we get

$$K' = \frac{1}{2} \sum_{\alpha, \beta} \gamma_{\alpha\beta} (M_{\alpha} - \mu_{\alpha})(M_{\beta} - \mu_{\beta}) + \frac{1}{2} \sum_{j, l} g_{jl} P_j P_l - \frac{i\hbar}{2} \sum_j s_j P_j - \frac{i\hbar}{2} \sum_{\alpha} (s'_{\alpha} + s''_{\alpha})(M_{\alpha} - \mu_{\alpha}). \quad (119)$$

All the terms of Eq. (119) linear in $M_{\alpha} - \mu_{\alpha}$ vanish when $\delta r^{(1)} \rightarrow 0$, but those linear in P_j do not. This fact can cause difficulties in practical

utilization of the Hamiltonian containing K' , and it is more convenient to replace the latter by an operator K'' , such that it does not contain the undesirable terms and, at the same time, is connected to K' by a similarity transformation. This transformation should make use of the Jacobian of the initial Cartesian coordinates with respect to the new ones we have chosen, as it takes place when passing to the normal coordinates.

9. Calculation of the Jacobian

The Jacobian of the initial Cartesian coordinates with respect to the new ones obviously is $|D|^{1/2}$, where D is the matrix given in Eq. (34). From Eq. (34) we get

$$\hat{D}_{mD} = \begin{vmatrix} ME_3 & 0 & 0 \\ 0 & \chi^{(n)} I'' C^{(n)} & \chi^{(n)} \chi^{(r)'}_{mA} \\ 0 & \chi_{mA}^{(r)'} C^{(n)} & T \end{vmatrix} \quad (120)$$

where

$$I'' = \chi^{(r)'}_{mA} \chi^{(r)'}_{mA}. \quad (121)$$

Equation (120) yields,¹⁶ in view of Eqs. (55c) and (76),

$$|\hat{D}_{mD}| = |D|^2 = \text{const} |C^{(n)}|^2 |T| |I'' - \kappa T \kappa|. \quad (122)$$

Since we are interested only in the factor depending on $r^{(1)}$, we will deal merely with $|I'' - \kappa T \kappa|$. To simplify this, let us consider also the inverse matrix

$$D^{-1} \hat{D}_{mD}^{-1} = \begin{vmatrix} M^{-1} E_3 & 0 & 0 \\ 0 & C^{(n)'} \Gamma C^{(n)'} & -C^{(n)'} \Gamma \kappa \\ 0 & -\kappa \Gamma C^{(n)'} & G + \kappa \Gamma \kappa \end{vmatrix}. \quad (123)$$

It follows from $\tilde{D} D (D^{-1} \tilde{\epsilon} D^{-1}) = E_{3n}$, in view of Eq. (61), that

$$I'' - \tilde{\kappa} T \kappa = \Gamma^{-1}. \quad (124)$$

Therefore, in view of Eqs. (122), (95), and (71b),

$$|D|\alpha|I'|; |D|^{-1}\alpha|G^{(r)}'|. \quad (125)$$

10. Calculation of K'' and the Hamiltonian

In this section we will need some results concerning canonically conjugate operators.^{17,18} That term is used for any operators $\hat{a}$ and $\hat{b}$ obeying

$$[\hat{a}\hat{b}] = c\hat{E} \quad (126)$$

where c is a constant and $\hat{E}$ is the unit operator. Operators P_j and q_j are canonically conjugate, c being equal to $-i\hbar$. Functions of canonically conjugate operators are noncommutative, and if there are N mutually independent pairs of canonically conjugate operators $\hat{a}_j$ and $\hat{b}_j$ for which the relations

$$[\hat{a}_j\hat{b}_k] = c\delta_{jk}\hat{E}; [\hat{a}_j\hat{a}_k] = [\hat{b}_j\hat{b}_k] = 0 \quad (127)$$

where $\hat{E}$ is the unit operator, are valid, then for the operators $\hat{\phi} = \phi(\hat{a}_1, \dots, \hat{a}_N, \hat{b}_1, \dots, \hat{b}_N)$ and $\hat{f} = f(\hat{a}_1, \dots, \hat{a}_N, \hat{b}_1, \dots, \hat{b}_N)$ we obtain

$$\hat{\phi}\hat{f} = \hat{f}\hat{\phi} + \sum_{l=1}^{\infty} \frac{c^l}{l!} \left(\frac{\partial^l \hat{f}}{\partial \hat{b}^l} \frac{\partial^l \hat{\phi}}{\partial \hat{a}^l} - \frac{\partial^l \hat{\phi}}{\partial \hat{b}^l} \frac{\partial^l \hat{f}}{\partial \hat{a}^l} \right) \quad (128)$$

where

$$\frac{1}{l!} \frac{\partial^l \hat{f}}{\partial \hat{b}^l} \frac{\partial^l \hat{\phi}}{\partial \hat{a}^l} = \sum_{l_1, l_2, \dots, l_N} (l_1! \dots l_N!)^{-1} \frac{\partial^l \hat{f}}{\partial \hat{b}_1^{l_1} \dots \partial \hat{b}_N^{l_N}} \frac{\partial^l \hat{\phi}}{\partial \hat{a}_1^{l_1} \dots \partial \hat{a}_N^{l_N}} \quad (129)$$

$(l_1 + \dots + l_N = l)$

When applying Eq. (128) to the calculation of

$$K'' = |G^{(r)'}|^{-1/2} K' |G^{(r)'}|^{1/2} \quad (130)$$

we will need the first and second order derivatives of $|G^{(r)'}|^{1/2}$ with respect to the q_j 's. We have, in view of Eq. (112), and (113a)

$$\frac{\partial |G^{(r)'}|^{1/2}}{\partial q_j} = \frac{1}{2} |G^{(r)'}|^{1/2} \text{Sp} I' \frac{\partial G^{(r)'}}{\partial q_j} = -\frac{1}{2} |G^{(r)'}|^{1/2} c_j \quad (131)$$

and, in view of the linearity of I' in the $\delta r^{(i)'}_s$,

$$\begin{aligned} \frac{\partial^2 |G^{(r)'}|^{1/2}}{\partial q_k \partial q_j} &= \frac{1}{4} |G^{(r)'}|^{1/2} \text{Sp} G^{(r)'} I'_{(k)} \text{Sp} G^{(r)'} I'_{(j)} \\ &+ \frac{1}{2} |G^{(r)'}|^{1/2} \text{Sp} G^{(r)'} I'_{(k)} G^{(r)'} I'_{(j)} = \frac{1}{2} |G^{(r)'}|^{1/2} \left(\frac{1}{2} c_k c_j + c_{kj} \right) \end{aligned} \quad (132)$$

where

$$c_{kj} = \text{Sp} G^{(r)'} I'_{(k)} G^{(r)'} I'_{(j)}. \quad (132a)$$

In Eq. (130) $|G^{(r)'}|^{1/2}$ is a function of the $\delta r^{(i)'}_s$ only, whereas the μ_α are functions of both the P_j and $\delta r^{(i)'}_s$. But, as it is seen from Eq. (128), we will not need the derivatives of μ_α with respect to q_j , since $|G^{(r)'}|$ does not depend on P_j . On the strength of Eqs. (131) and (132), the transformation given in Eq. (130) merely adds to K' some linear terms and functions. In particular, the linear terms resulting from $\frac{1}{2} \sum_{j,l} g_{jl} P_j P_l$ are, in view of Eqs. (128), (113), and (131),

$$\frac{i\hbar}{2} \sum_{l,j} c_{kl} g_{lj} P_j = \frac{i\hbar}{2} \sum_j g_{jj} P_j. \quad (133)$$

These obviously cancel the corresponding linear terms in K' . The term quadratic in P_j yields also, in view of Eq. (132),

$$V_1' = -\frac{\hbar^2}{4} \sum_{l,j} g_{lj} \left(\frac{1}{2} c_l c_j + c_{lj} \right). \quad (134)$$

From the term linear in P_j we get, in view of Eq. (131),

$$V_1'' = \frac{\hbar^2}{4} \sum_j s_j c_j = \frac{\hbar^2}{4} \sum_{l,j} g_{lj} c_l c_j. \quad (135)$$

We get linear terms, which are due to the term quadratic in $M_\alpha - \mu_\alpha$, from

$$\frac{i\hbar}{4} \sum_{\alpha,\beta} \gamma_{\alpha\beta} \sum_j \frac{\partial}{\partial P_j} (M_\alpha - \mu_\alpha) (M_\beta - \mu_\beta). \quad (136)$$

In view of Eqs. (92), (74a), and (128),

$$\begin{aligned} \frac{\partial (M_\alpha - \mu_\alpha) (M_\beta - \mu_\beta)}{\partial P_j} &= -\kappa_{j\alpha} (M_\beta - \mu_\beta) - (M_\alpha - \mu_\alpha) \kappa_{j\beta} \\ &= -[\kappa_{j\alpha} (M_\beta - \mu_\beta) + \kappa_{j\beta} (M_\alpha - \mu_\alpha)] - i\hbar \sum_l \kappa_{j\beta}^{(l)} \kappa_{l\alpha} \end{aligned} \quad (137)$$

where

$$\kappa_{j\beta}^{(l)} = \frac{\partial \kappa_{j\beta}}{\partial q_l}. \quad (138)$$

Therefore, Eq. (136) yields

$$\begin{aligned} -\frac{i\hbar}{2} \sum_{\alpha,\beta} \gamma_{\alpha\beta} \sum_j \kappa_{j\beta} (M_\alpha - \mu_\alpha) + \frac{\hbar^2}{4} \sum_{\alpha,\beta} \gamma_{\alpha\beta} \sum_{j,l} c_j \kappa_{j\beta}^{(l)} \kappa_{l\alpha} \\ = -\frac{i\hbar}{2} \sum_\alpha s_\alpha'' (M_\alpha - \mu_\alpha) + V_2 \end{aligned} \quad (139)$$

where

$$s_\alpha'' = \sum_j \sum_l \gamma_{\alpha\beta} \kappa_{j\beta}^{(l)} \kappa_{l\alpha} \quad (140)$$

and

$$V_2 = \frac{\hbar^2}{4} \sum_{\alpha,\beta} \sum_{l,j} \kappa_{j\beta}^{(l)} \kappa_{l\alpha} \gamma_{\alpha\beta} c_j. \quad (141)$$

From the same quadratic term we also obtain, in view of Eqs. (128), (132), and (137),

$$\begin{aligned} V_3 &= -\frac{\hbar^2}{4} \sum_{\alpha, \beta} \gamma_{\alpha\beta} \sum_{j, l} (\kappa_{ja} \kappa_{lb} + \kappa_{la} \kappa_{jb}) \left(\frac{1}{2} c_l c_j + c_{lj} \right) \\ &= -\frac{\hbar^2}{2} \sum_{\alpha, \beta} \sum_{j, l} \gamma_{\alpha\beta} \kappa_{ja} \kappa_{lb} \left(\frac{1}{2} c_l c_j + c_{lj} \right). \end{aligned} \quad (142)$$

At last, terms linear in $M_a - \mu_a$ yield

$$V_4 = -\frac{\hbar^2}{2} \sum_a (s'_a + s''_a) \sum_j c_j \kappa_{ja}. \quad (143)$$

Combining all the above results, we can finally write the rotation-vibration Hamiltonian $H'' = K'' + V$ as

$$\begin{aligned} H'' &= \frac{1}{2} \sum_{\alpha, \beta} \gamma_{\alpha\beta} (M_a - \mu_a) (M_\beta - \mu_\beta) + \frac{1}{2} \sum_{j, l} g_{jl} p_j p_l \\ &\quad - \frac{i\hbar}{2} \sum_a (M_a - \mu_a) + V' + V \end{aligned} \quad (144)$$

where

$$s_a = s'_a + s''_a + s'''_a \quad (145)$$

and

$$\begin{aligned} V' &= V'_1 + V''_1 + V_2 + V_3 + V_4 \\ &= \frac{\hbar^2}{4} \left[\sum_{j, l} \left(\sum_{\alpha, \beta} \kappa_{j\alpha}^{(l)} \kappa_{l\alpha} \gamma_{\alpha\beta} - \sum_a (s'_a + s''_a) \kappa_{ja} \right) c_j \right. \\ &\quad \left. + \sum_{j, l} \left(\frac{1}{2} g_{jl} - \sum_{\alpha, \beta} \kappa_{ja} \kappa_{lb} \gamma_{\alpha\beta} \right) c_j c_l - \sum_{j, l} (g_{jl} + 2 \sum_{\alpha, \beta} \kappa_{ja} \kappa_{lb} \gamma_{\alpha\beta}) c_{jl} \right]. \end{aligned} \quad (146)$$

Here s'_α , s''_α , and s'''_α are as given in Eqs. (105), (118), and (140), respectively. The rest of notation remains the same as before.

11. Discussion

The coefficients $\gamma_{\alpha\beta}$ and s_α in Eq. (144), as well as V' in it, can be expressed explicitly as functions of Cartesian displacements of atoms in the rotating coordinate system and do not depend on the choice of internal coordinates. Therefore, they can be calculated in a system of internal coordinates the most appropriate for every particular case, irrespective of what a system of internal coordinates could be chosen for the computation of molecular vibrations.

No restrictions in the magnitudes of the atomic displacements have been made in deriving the new Hamiltonian; therefore, it is exact. In contrast with this Hamiltonian, the conventional one is valid only for small enough atomic displacements due to the fact that they are represented as linear combinations of normal coordinates.

The new Hamiltonian can be easily represented in the form of a differential operator, by making use of Eqs. (91), (92), (71a), and (5). This fact releases one from the necessity of utilizing the only computational method used by now, namely, the perturbation one, and allows one to hope that some other methods of approximate calculation could be used more successfully. Even if one chooses the perturbation method, the new Hamiltonian seems to be simpler for applications, since it has an explicit form and all its coefficients can be expressed explicitly.

In application of the new rotation-vibration Hamiltonian to the particular case of linear molecules, if the molecular axis is chosen as the

z-axis of the rotating coordinate system, then $\chi = 0$, the $R_x^{(i)}$ and $R_y^{(i)}$ are zeros in Eq. (30) and everywhere else, because of which I and I' as well as $G^{(r)}$, $G^{(r)'}$, and Γ are 2 by 2 diagonal matrices with equal diagonal elements in each of them. The Hamiltonian as given in Eq. (144) is thereby significantly simplified.

I will emphasize, too, that in deriving the new Hamiltonian the only supposition that has actually been made is the existence of an equilibrium configuration for a molecule. No Eckart's conditions¹⁹ proved to be necessary anywhere in the deduction.

In the process of the derivation, the equations of §4 proved to be very helpful. The method of calculation of the Jacobian needed (§9) as well as the method used for the similarity transformation of K' (§10) may be of particular interest too.

The following advantages of the new rotation-vibration Hamiltonian over the conventional one are obvious: (1) the exactness of the former, in contrast with the approximate nature of the latter; (2) the explicit form of the former, in contrast with the tangled form of the latter; (3) the independence of all the terms of the former but V of the force coefficients, whereas all the terms of the latter except V are implicit functions of those; (4) the possibility of applying approximate calculation methods other than the perturbation one to the former, whereas that is impossible to do for the latter.

Certainly, some other advantages of the new Hamiltonian over the conventional one would be revealed in practical application of the former to the computation of various particular rotation-vibration spectra. The new rotation-vibration Hamiltonian can prove to be of special importance for

computation of molecular spectra in the case of large rotation or vibration quantum numbers, in particular, for computation of spectra of molecules near their dissociative limits. But I do not foresee cases when the conventional rotation-vibration Hamiltonian could have any advantage over the new one.

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6. See, for instance, H. Goldstein, Classical Mechanics, Cambridge, 1950, p. 109.
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