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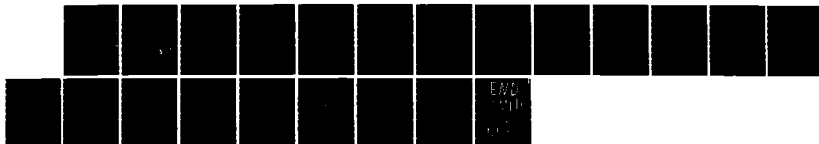
AN EFFICIENT METHOD FOR SOLVING QUANTUM LIOUVILLE  
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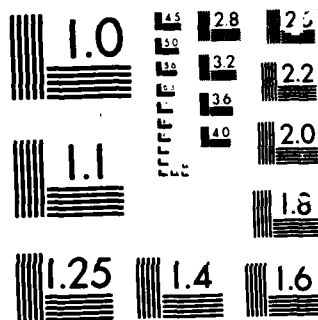
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AN EFFICIENT METHOD FOR SOLVING QUANTUM LIOUVILLE  
EQUATION: APPLICATIONS TO ELECTRONIC ABSORPTION  
SPECTROSCOPY

by

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Chem. Phys. Lett., submitted (1985)

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AN EFFICIENT METHOD FOR SOLVING QUANTUM LIOUVILLE EQUATION:  
APPLICATIONS TO ELECTRONIC ABSORPTION SPECTROSCOPY

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## ABSTRACT

We examine a method for solving Liouville's equation, consisting of successive application of short time propagators which are evaluated by using fast Fourier transforms. The method is examined numerically by computing electronic absorption spectra. The procedure is very efficient when applied to the study of short time dynamics of systems whose quantum degrees of freedom are spatially localized. .

## I. INTRODUCTION

We propose in this article a method for solving the equation

$$i\hbar \frac{\partial \rho}{\partial t} = \pm \{H_u \rho - \rho H_l\} \quad , \quad (1)$$

which describes a variety of physical processes. If the positive sign is taken and  $H \equiv H_u \equiv H_l$  is the Hamiltonian, Equation (1) is the quantum Liouville equation (QLE) which gives the time evolution of the non-equilibrium density matrix  $\rho(t)$ . Taking the negative sign and  $H_u = H_l$  leads to Heisenberg equation for the temporal evolution of an operator  $\rho(t)$ . The form with different Hamiltonians  $H_u \neq H$  is useful for the computation of the electronic absorption<sup>1</sup> spectrum

$$\Sigma(\omega) \equiv (1/\pi) \text{Re} \int_0^{\infty} dt e^{i\omega t} e^{-\gamma t} \text{Tr} \rho(t) \quad . \quad (2)$$

Here

$$\rho(t) = \exp(-iH_u t/\hbar) \rho(0) \exp(iH_l t/\hbar) \quad (3)$$

and

$$\rho(0) = \mu(r) \exp(-\beta H_l) / Z_1 \quad (4)$$

with

$$Z_1 = \text{Tr}(\exp(-\beta H_l)) \quad .$$

The two Hamiltonians

$$H_l = -(\hbar^2/2m)\nabla_r^2 + V_l(\vec{r}) + E_0 \text{ and } H_u = -(\hbar^2/2m)\nabla_r^2 + V_u(\vec{r})$$

(5)

represent the nuclear motion in the "upper" and "lower" electronic states and  $\mu(\vec{r})$  is the transition dipole moment between these states.  $V_l(R)$  and  $V_u(R)$  are the potential energy surfaces of the two states and  $E_0$  is the energy gap between them. The Equation (2) is a rearrangement of the usual expression<sup>2-4</sup> that gives the absorption spectrum in terms of the Fourier transform of the dipole-dipole correlation function. Since  $\rho(t)$  defined by Eq. (2) satisfies equation (1) (with the plus sign) we can calculate absorption spectra by solving Eq. (1) with the initial condition given by Eq (4).

Thus it should be clear that the development of an efficient method for solving Eq. (1) is of importance for non-equilibrium statistical mechanics (transport theory and thermal rates) and the spectroscopy of thermalized molecules (i.e. prepared in an oven or imbedded in a condensed medium held at constant temperature).

We propose and test here a method which applies to the present problem ideas developed by Fleck, Morris and Feit (FMF)<sup>5</sup> for solving Maxwell's equations.

## II. THE METHOD OF SOLUTION

In coordinate representation equation (1) can be written as

$$i\hbar \partial \rho(r, r'; t) / \partial t = \{ -(\hbar^2/2m)(\partial^2/\partial r^2) + (\hbar^2/2m)(\partial^2/\partial r'^2) + V_u(r) - V_l(r') \} \rho(r, r'; t) \quad (6)$$

For a very short time  $\tau$  we can write

$$\rho(r, r'; t+\tau) = W_u(r, \tau) W_l^*(r'; \tau) \rho(r, r'; t) \quad (7)$$

where

$$W_u(r, \tau) = \exp\{(i\hbar\tau/4m)\nabla_r^2\} \exp(-i\tau V_u(r)/\hbar) \exp\{(i\hbar\tau/4m)\nabla_r^2\} \quad (8)$$

is the "split propagator" used by FMF.<sup>5</sup>  $W_l^*(r'; \tau)$  is obtained from Eq. (8) by replacing  $V_u(r)$  with  $V_l(r)$ ,  $\nabla_r$  with  $\nabla_{r'}$ , and  $i$  with  $-i$ .

For  $n$  small time steps we have

$$\rho(r, r'; n\tau) = [W_u(r, \tau) W_l^*(r', \tau)]^n \rho(r, r'; 0) = (G(r, r'; \tau))^* [U_u(r; \tau) U_l(r; \tau)]^{n-1} G(r, r'; \tau) \rho(r, r'; 0) \quad (9)$$

where

$$G(r, r'; \tau) = \exp\{(i\hbar\tau/4m)(\nabla_r^2 - \nabla_{r'}^2)\} \quad (10)$$

and

$$U_u(r, \tau) = \exp\{(i\hbar\tau/2m)\nabla_r^2\} \exp(-i\tau V_u(r)/\hbar) \quad (11)$$

$U_l(r'; \tau)^*$  is obtained from Eq. (11) by replacing  $V_u(r)$  with  $V_l(r')$ ,  $\nabla_r$  with  $\nabla_{r'}$ , and  $i$  with  $-i$ .

We compute  $\rho(r, r'; n\tau)$  by using Eq. (9). The more difficult part is the calculation of the effect of the operators containing exponentials of the form  $\exp((i\tau\hbar^2/2m)\nabla_r^2)$ . To illustrate the procedure we show in detail the calculation of

$$X(r) \equiv U_u(r, \tau)f(r, r') , \quad (12)$$

where  $f(r, r')$  is a known function and  $U_u(r, \tau)$  is given by Eq. (11).

Using Eq. (11) and simple manipulations based on the representation theory we can write

$$X(r) = \int dk_2 dr_1 \langle r_2 | k_2 \rangle \exp\{-i(\hbar^2 k_2^2 \tau / 2m)\} \langle k_2 | r_1 \rangle \exp\{-i\tau V(r_1)/\hbar\} f(r_1, r') \quad (13)$$

Here we have used the momentum representation in which the Laplacian is diagonal. The price paid for this easy diagonalization is that we must perform the two integrals over  $dr_1$  and  $dk_2$ . Fortunately, since  $\langle k_2 | r_1 \rangle$  and  $\langle r | k_2 \rangle$  are plane waves, the integrals are a Fourier transform and an inverse Fourier transform, which can both be efficiently performed by using a fast Fourier transform (FFT) routine.<sup>6</sup>

This method can be used for computing the effect of the operators  $G$  and  $U$ . Repeated application for  $n$  small time steps  $\tau$ , as indicated in Eq. (9), gives the evolution of  $\rho(r, r'; t)$  from  $\rho(r, r'; 0)$  to  $\rho(r, r'; n\tau)$ .

The number of operations and the magnitude of the errors can be analyzed to some extent, to establish the conditions under which this method is most efficient. The error made by using the "split propagator" for a short time  $\tau$ , is of order  $\tau^3$ ; if we were to use  $\rho(r, r'; n\tau) = (U_u(r, \tau)U_e(r'; \tau))^n \rho(r, r'; 0)$ , like in the path integral theory<sup>7</sup>, the error would be of order  $\tau^2$ . Furthermore, if the dependence of  $\rho(r, r'; t)$  on  $r$  and  $r'$  can be adequately described on a  $N$  point grid, then each FFT requires, roughly,  $N \ln_2 N$  operations per coordinate; the equations discussed here have two coordinates per degree of freedom. The number of grid points  $N$  is  $L/l$  where  $L$  is the length over which  $\rho(r, r'; t)$  is localized, and  $l$  is the shortest length scale over which the  $\rho(r, r'; t)$  changes. Thus for each time step the number of operations required to perform the necessary FFTs is  $2(N \ln_2 N)^2$ . The calculation of  $U$  also requires  $N$  multiplications with  $\exp\{-iV_u(r)\tau/\hbar\}$ , one for each grid point. The exponentials  $\exp\{-i\tau V(r)/\hbar\}$  are calculated once, at the beginning. Since two such multiplications are required per time step, the total number of such operations is  $2N$ . The same number of multiplications are required for the terms  $\exp\{-i\hbar^2 k_n^2/2m\}$ , where  $k_n$  are the grid points in the momentum space; these exponentials are also computed once, at the beginning, since the grid points are not changed during the calculation.

The total number of operations per time step is thus

$2(N \ln_2 N)^2 + 4N$ . The number of time steps is determined by the physical characteristics of the problem at hand. In the case of electronic absorption spectrum, which is used for illustration in this article, the time step must be smaller than  $2\pi/\delta$ , where  $\delta$  is the width of the Franck-Condon envelope, and the length of time that  $\rho(t)$  must be propagated is of order  $\gamma^{-1}$ , where  $\gamma$  is the width of the narrowest line that we want to resolve.<sup>8</sup>

### III. The Calculation of Electronic Absorption Spectra

To test the method described here we have applied it to the problem of electronic absorption by a model diatomic molecule whose ground and excited state potential energies are harmonic oscillators of equal frequency  $\omega_0 = 0.01 \text{ a.u.} = 2.72 \text{ meV} = 2176 \text{ cm}^{-1}$ , whose equilibrium positions are displaced by a length  $\delta x = 0.33 \text{ a.u.} = 0.16 \text{ \AA}$ , and whose reduced mass is that of a proton.

We chose this problem because the exact result is known.<sup>9</sup> Since the spectrum and the Hamiltonians have all the features expected in a realistic problem, the model provides an adequate test of the method of computation.

The calculation starts with the assumption that the transition dipole  $\mu(r)$  is independent of  $r$ . There is no additional difficulty in using a function for  $\mu(r)$ ; we used a constant since exact results are available for that case. The equilibrium density matrix  $\exp(-\beta H_1)/Z_1$  was calculated in coordinate representation by using a FFT method proposed by Hellsing, Nitzan and Metiu.<sup>10</sup> This provides the exact initial value  $\rho(r, r'; t=0) = \langle r | \exp(-\beta H_1) | r' \rangle / Z_1$ . This is propagated by using (9) and the method described above. The spectrum  $\Sigma(\omega)$  is obtained from Eq. (2). Since the band edge is determined by the energy gap  $E_0$  between the states (i.e. the electronic excitation energy) we can shift the spectrum arbitrarily on the frequency scale without causing confusion.

The length of time  $T$  for which we need to propagate  $\rho(r, r'; t)$  is set by the magnitude of  $\gamma$  appearing in Eq. (2). Here

$\gamma$  is the rate of the slowest process causing the decay of the upper state amplitude, and it could be the natural line width,<sup>11</sup> the rate of a radiationless transition, predissociation, or photodissociation in an additional degree of freedom whose dynamics is not explicitly included;<sup>4,12</sup> one can also think of  $\exp(-\gamma t)$  as a "filter function"<sup>6</sup> used to avoid the numerical difficulties associated with computing 6 functions numerically. In the latter case  $\gamma$  must be smaller than the transition frequencies which one intends to resolve when the spectrum is computed. We use throughout the paper  $\gamma T = 5$  with  $\gamma = 0.028$  a.u. ( $\gamma/\omega_0 = 0.28$ ).

The dependence of the spectrum on the number of spatial grid points is illustrated in Fig. 1. The result obtained with 32 grid points is exact, that for 16 points is reasonably accurate, while the use of eight points leads to serious errors.

The sensitivity to the number of spatial grid points appears because the height of each peak and the total width of the spectrum is determined by the magnitude of the Frank-Condon factors, which are wave function overlaps. A poor spatial grid will result in erroneous high energy Franck-Condon factors, since the highly excited wave functions appearing in them have a larger number of spatial oscillations and these are not well described on a coarse grid. When an insufficient number of grid points is used the low frequency part of the spectrum is usually not as bad as the high frequency one.

In Figure 2 we show the dependence of the spectrum as a function of the number of time steps. The results obtained by

using 1000 time steps are exact, those using 25 steps are adequate and the error made by this dramatic lowering of the number of steps occurs mainly at the low intensity side of the spectrum, where the experiments are also likely to be less accurate.

In Figure 3 we show the temperature dependence of the spectra. The increase in temperature causes the growth of the hot bands and a corresponding decrease in the peaks which are present at zero temperature.

#### IV DISCUSSION

Both actual calculations and estimates of the number of operations indicate that the present method of solving the Liouville equation is very efficient if: (a) the density matrix, in coordinate representation, is spatially localized; (b) the density matrix changes with position over a sizable space scale; (c) the duration of the dynamic process of interest is short (in spectroscopy this means that the Franck-Condon envelope is broad); (d) the required time step is small (in spectroscopy this means that the ratio between the width of the narrowest line and the width of the envelope is large); (e) the problem has few quantum degrees of freedom.

Even though a theory based on Liouville's equation is more general than one provided by the Schrodinger equation, such a formulation is not always required, nor is it generally advisable. In cases when  $k_B T$  is comparable to the excitation energy of the quantum system, it is computationally more efficient to propagate the few states which are thermally populated and average the

results with a quantum Boltzman factor. This happens because the dimensionality of the Liouville equation is twice that of Schrodinger equation.

When we deal however with molecules imbedded in a condensed medium, whose molecules are held at constant temperature and are propagated by classical mechanics, the situation is not so clear cut.

Under these circumstances the initial conditions for the quantum degrees of freedom are determined in two steps: First we use the Monte Carlo method to establish the position of the atoms of the medium and to compute the potential energy of molecule in the presence of the medium; then we determine the quantum density matrix of the molecule for these potentials. Under these conditions the molecular wave functions are much more difficult to determine than the equilibrium density matrix. Therefore, since the initial state is defined by the density matrix the subsequent time evolution (caused by the electromagnetic field and the classical motion of the molecules of the medium) and the spectrum corresponding to it, must be calculated by solving the Liouville equation. The same is true for rate or transport processes.

The reason why the present method might play an important role in future developments is that it is so efficient that such calculations - which require the calculation of the quantum evolution of the molecule's density matrix for each Monte Carlo configuration of the molecules in the medium - are possible if the problem has one or perhaps two degrees of freedom which are

spatially localized, and the process is completed in a reasonably short time.

**Acknowledgements:**

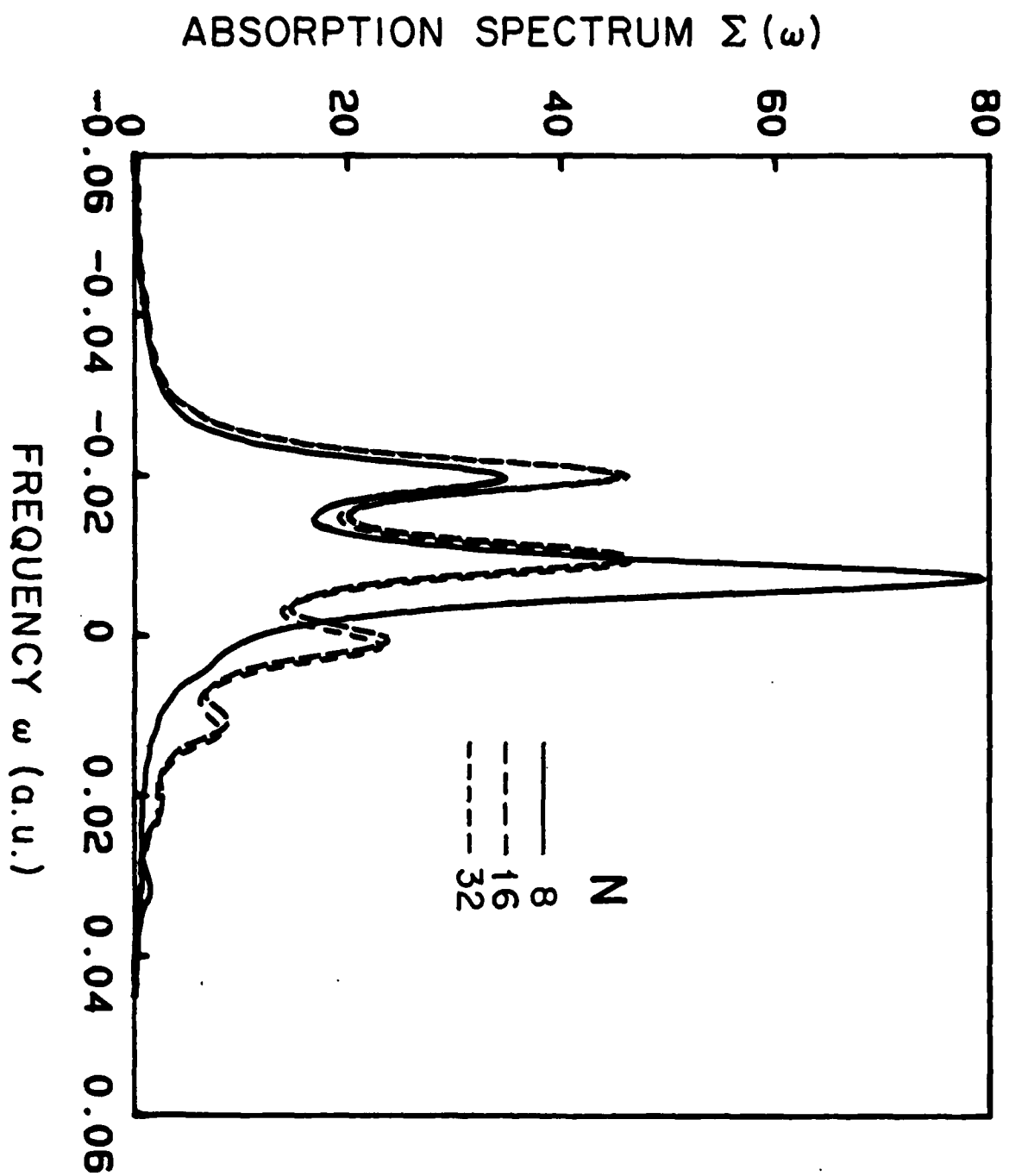
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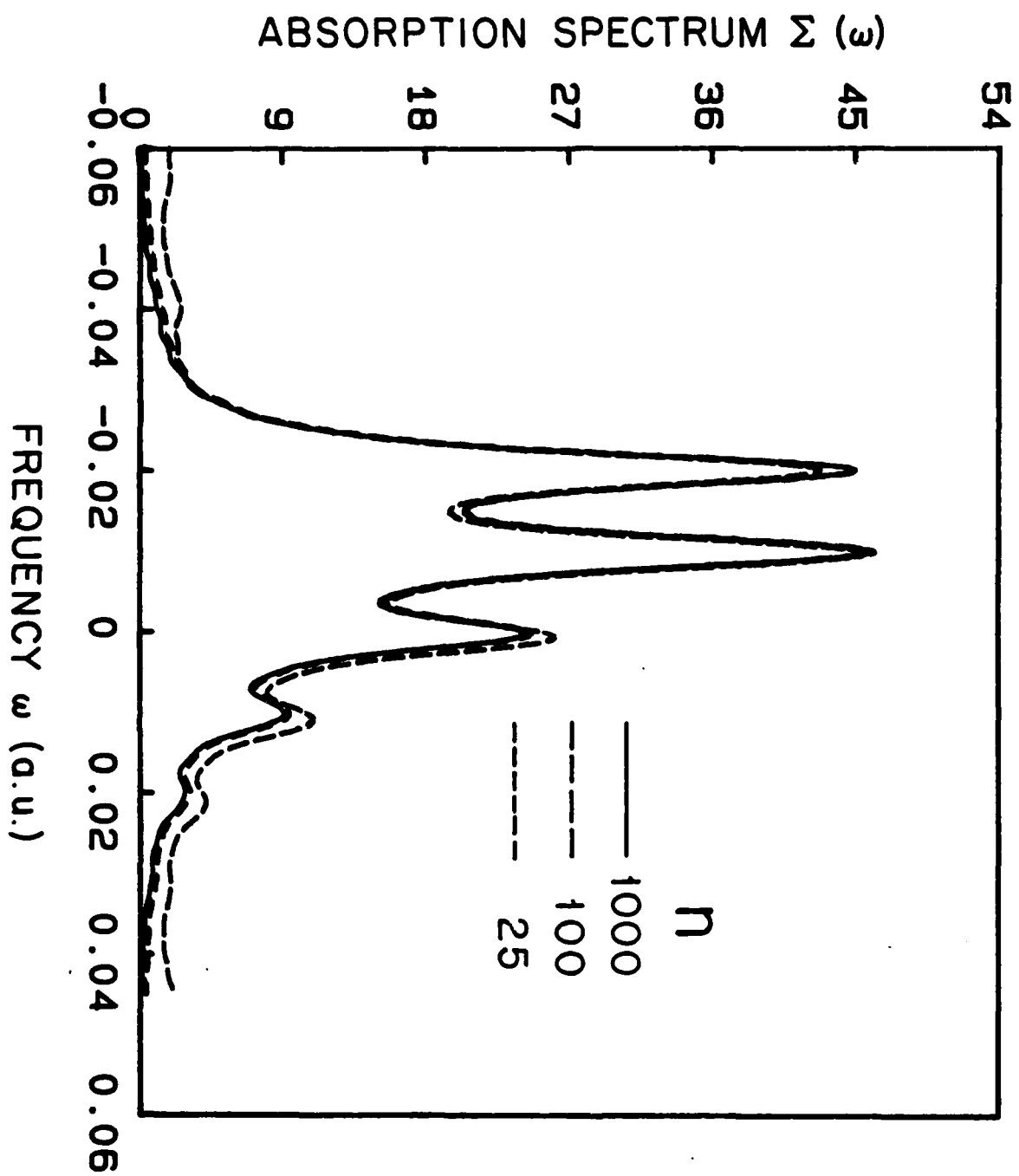
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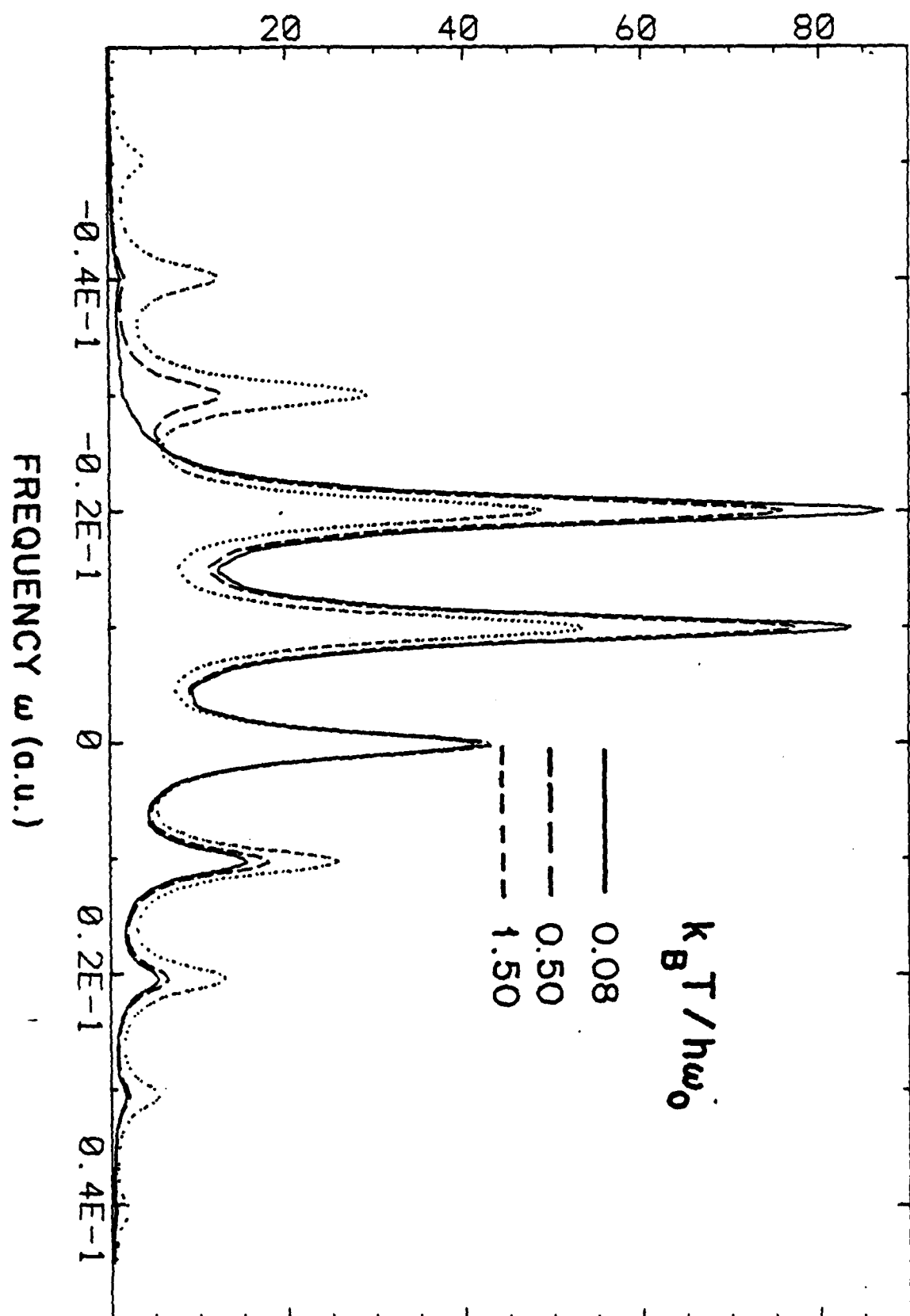
# FIGURE CAPTIONS

- Fig. 1. The dependence of the computed spectrum on the number of points  $N$  in the spatial grid. Full line  $N=8$ ; dotted lines  $N=16$ ; dashed line  $N=32$ . We have used 1000 time steps,  $\hbar\omega_0/k_B T = 12.5$ ,  $\omega_0 = 272 \text{ meV} = 0.01 \text{ a.u.}$ ,  $\gamma/\omega_0 = 0.28$ .
- Fig. 2. Spectra computed with various time steps: full line, 1000 steps; dashed line, 100 steps; and dotted line, 25 steps. The spatial grid has 64 points. The parameters are those used in Figure 1.
- Fig. 3. Spectra at various temperatures. The parameters are those used in Fig. 1.





# ABSORPTION SPECTRUM $\Sigma(\omega)$



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