Effect of temperature on multiphoton dissociation of CF_3Br; determination of the initial energy of the dissociated molecules

V. B. Laptev, E. A. Ryabov, and N. P. Furzikov

Spectroscopy Institute, USSR Academy of Sciences

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The temperature dependence of the multiphoton dissociation (MPD) of trifluororbromomethane is investigated at various excitation frequencies. It is shown that when CF_3Br is excited at a frequency detuned towards longer wavelengths (-0.5–$41.5\ cm^{-1}$) from the center of the linear absorption band, the principal contributions to the MPD yield are made by molecules with vibrational energies that exceed the average thermal vibrational energy. These energies are found to range from 450 to 2500 cm^{-1}. The temperature and frequency dependence of the MPD selectivity are explained.

1. INTRODUCTION

A characteristic feature of multiphoton excitation (MPE) of molecules by an *IR* laser is the formation of at least two populations consisting respectively of strongly excited (vibrationally "hot") and weakly excited (vibrationally "cold") molecules (see, e.g., Ref. 1). A qualitative explanation of this experimental fact is that the resonant IR radiation interacts differently with the different vibrationally excited levels over which the molecules are distributed at finite (usually room) gas temperature. A quantitative interpretation of these results, especially a calculation of the fraction q of the "hot" molecules, is at present difficult. In fact, this calls for knowledge of the states from which the molecules are drawn into the MPE process and in what manner, but the available pertinent data are insufficient. In addition, this information is needed in principle to understand the mechanism that makes multiphoton dissociation (MPD) selective, which in turn is of great practical importance for laser isotope separation.

Direct experiments on spectroscopic probing of excited molecules have shown that in MPE many states can interact simultaneously with the field, as is the case, e.g., for SF_6.[2] These experiments, however, were unable to identify specifically the vibrational-rotational states that participate in the MPE process, nor the probability of this participation.

Since the initial energy distribution of the molecules is determined by the temperature, a large number of experimental investigations have been made of its influence on the parameters of the multiphoton excitation and dissociation. They have shown that lowering the temperature makes the MPE spectrum narrower, and changes the yield and selectivity of the MPD. This behavior was attributed to narrowing of the rotational distribution of the vibrational ground state[3–5] and to a decrease of the population of the low-lying vibrational states.[6–9] Even these experiments, however, while essentially confirming the influence of the initial energy distribution of the molecules on the parameters of their MPE, yield no unambiguous information on the states that make the main contribution to this process. Our study was aimed at determining, with the CF_3Br molecule as the example, those energy states which make the main contribution to the formation of the hot-molecule ensemble, and thus determine the MPD yield and selectivity and their dependence on the excitation conditions.

We report below the experimental results. To the best of our knowledge, we have determined directly, for the first time ever, the initial energy of the dissociating molecules. The results also explain the experimentally observed dependence of the MPD selectivity on the gas temperature and on the exciting laser-radiation frequency.

2. EXPERIMENT

In our opinion, one of the simplest methods of determining the energies of states that interact with a field is to study the temperature dependences of the MPD yields. This approach was used in Ref. 10, where the vibrational-states energy of the molecules interacting with cw CO_2 laser radiation was determined by measuring the temperature dependences of the linear absorption.

In the case of multiphoton excitation we can write for the MPD yield β the expression

$$\beta=\sum_{E} P_{\rm diss}(E)N(E), \tag{1}$$

where $N(E)$ is the population of a level with energy E, and $P_{\rm diss}(E)$ is the corresponding MPD probability.

If the excitation is from a narrow energy interval ΔE, i.e., for $\Delta E \ll E$, expression (1) takes the following simpler form

$$\beta=P_{\rm diss}(E)\sum_{\Delta E} N(E)=P_{\rm diss}(E)\rho(E)\Delta E Z_{\rm vib}^{-1}Z_{\rm rot}^{-1}e^{-E/kT}, \tag{2}$$

where $\rho(E)$ is the average density of states in the interval ΔE, while $Z_{\rm rot}$ and $Z_{\rm vib}$ are respectively the rotational and vibrational partition functions.

Taking logarithms and changing notation, we get

$$\ln(\beta Z_{\rm vib}Z_{\rm rot})={\rm const}-ET^{-1}. \tag{3}$$

Consequently, if the molecules are drawn into the MPD from a sufficiently narrow level band, the initial energy E of

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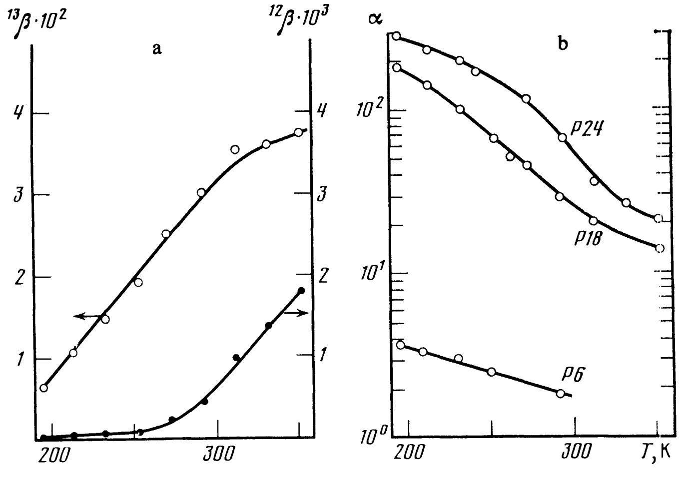

FIG. 1. a) Dissociation yields $^{12}\beta$ and $^{12}\beta$ of $^{13}CF_3Br$ and $^{12}CF_3Br$ vs temperature T for the P24 line. CF_3Br pressure 0.5 Torr, exciting-radiation energy density $\Phi = 2.6\ J \cdot cm^{-2}$. b) MPD selectivity α vs. temperature T for different excitation frequencies. Energy density $\Phi = 2.6\ J \cdot cm^{-2}$

the dissociated molecules can be determined from the slope of the function $\ln(\beta Z_{vib} Z_{rot}) = f(T^{-1})$.

We chose for the experiment the CF_3Br molecule with natural carbon isotopic composition; the MPD of this molecule has been studied in detail.[11] It is known, in particular that at room temperature and at a pressure $p_{CF_3Br} \leqslant 0.5$ Torr the MPD quantum efficiency of this molecule is $\varphi = D\beta/\bar{\varepsilon} \lesssim 1$ (here D is the molecule dissociation energy, and $\bar{\varepsilon}$ is the average absorbed energy; at the same time, the dissociation yield is only a few percent. This indicates that a small fraction of the molecules participates effectively with the field, so that the approach described above can be regarded as valid.

In the experiment we determined the temperature dependence of the dissociation yields $^{12}\beta$ and $^{13}\beta$ of $^{12}CF_3Br$ and $^{13}CF_3Br$, respectively, for several laser-radiation frequencies. We used a standard mass-spectroscopy procedure to measure the MPD yields (see, e.g., Ref. 1) The MPD selectivity was defined as the yield ratio $\alpha = {}^{13}\beta/{}^{12}\beta$. To prevent the possible recombination of the product radicals CF_3 and Br the experiments were performed with a 25:1 mixture of CF_3Br and O_2. The O_2 content was sufficient to convert all the CF_2 radicals into COF_2, as monitored by the absence of the competing C_2F_6 reaction. At all temperatures, the CF_3Br pressure was constant at 0.5 Torr, at which pressure the influence of V-V exchange on the MDP can be neglected.[11] The temperature was varied from 193 to 353 K in steps $T = 20$ K. The emission frequencies 1058.95, 1048.66, and 1043.16 cm^{-1} (the P6, P18, and P24 lines of the CO_2 laser) were chosen so that they spanned uniformly a wide interval of detuning from the linear-absorption band center, with allowance for a 26.2 cm^{-1} isotope shift. Thus, the frequencies for the $^{13}CF_3Br$ molecule fell in the Q branch of the ν_1 band and at the center of the MPD profile. The frequencies for $^{12}CF_3Br$ ended up on the far long-wave edge of both the linear-absorption band and of the MPD profile.

The radiation energy density was constant, $\Phi = 2.6\ J/cm^2$. The pulse had a standard waveform: a peak of ~70 ns at half-maximum and a tail ~500 ns at half-maximum, with approximately equal shares of the energy.

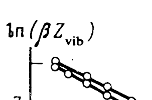

FIG. 2. Plots of $\ln(^{13}\beta Z_{vib})$ (light circles) and $\ln(^{13}\beta Z_{vib})$ (dark circles) versus T^{-1}. The circles mark the experimental points and the lines are the calculated curves.

3. EXPERIMENTAL RESULTS

Figure 1a shows the temperature dependence of the MPD yields $^{13}\beta$ and $^{12}\beta$ of the two isotopes for the P24 line. Similar curves were obtained for the two other lines. Depending on frequency, when the temperature is raised from 193 to 353 K the yields change by a factor 2–8 for $^{13}CF_3Br$ and 4–100 for $^{12}CF_3Br$. Note that the curves are different for the two isotopes. This makes the dissociation selectivity α depend on temperature, as seen in Fig. 1b. The selectivity decreases when the temperature is lowered and the radiation frequency is displaced from the center of the linear absorption band towards the red, reaching ~270 for the P24 line at $T = 193$ K.

The following additional assumptions were made when the results were reduced by the procedure described in Sec. 2. Expression (3) does not determine the vibrational and rotational components of the total energy E of the molecules that interact with the field. It can be concluded, however, from the experiments[11] which examined the influence of the rotational relaxation on the increase of the CF_3Br MPD yields when a buffer gas is added, that the field interacts with an appreciable fraction $q_{rot} \gtrsim 0.15$–0.20 of the population of the rotational sublevels of the resonant vibrational states. This permits an estimate of the average rotational energy

$E_{\rm rot}$ of these states, which should not differ greatly from the average thermal energy at such large $q_{\rm rot}$. It is less than 500 $\rm cm^{-1}$ even if all the resonant rotational sublevels are in the tail of the rotational distribution.

We can now use Eq. (3) to determine the initial vibrational energies $E_{\rm vib}$. Taking the above estimate of $E_{\rm rot}$ into account and neglecting the influence of the temperature dependences of the resonant rotational sublevel populations on the slope of the temperature dependence, we obtain from (3)

$$\ln(\beta Z_{\rm vib}) = {\rm const} - E_{\rm vib} T^{-1}. \quad (4)$$

The maximum error of the slope of the plot of (4) in this approach is less than ± 80 $\rm cm^{-1}$, a value comparable with the experimental error.

Reduction of the experimental data in accordance with Eq. (4) yielded the plots of $\ln(\beta Z_{\rm vib}) = f(T^{-1})$ shown in Fig. 2. Within the limits of error, all are straight or piecewise straight lines. The kinks observed for $^{12}\rm CF_3Br$ on the P18 and P24 lines are evidence that molecules from two groups of states with different energies are excited simultaneously. The starting energies, which are listed in Tabel I, were calculated from the slopes of the straight lines. Note, first, that all the values obtained exceed the average thermal vibration energy. Second, the farther the radiation wavelength is shifted from the linear-absorption band towards the red, the higher the energies of the states from which the molecules are effectively excited.

4. DISCUSSION

It follows from (2) that when the molecules are excited from a narrow energy interval the MPD is proportional to the equilibrium population of this interval. The first test of the validity of our procedure is therefore to compare the absolute values of the observed yields and population in a certain energy interval ΔE. This was done by numerically calculating the temperature dependence of the Boltzmann vibrational population in a ΔE interval with an average equal to the starting energy. Choosing $\Delta E = 100\text{–}150\ \rm cm^{-1}$, we found that the fraction of the molecules in this interval agrees with the observed values of the dissociation yield, i.e., $\beta = A\Delta N(E)$, where $A \approx 0.8$ on the P24 and P18 lines for $^{13}\rm CF_3Br$ and $A \approx 0.16$ for $^{12}\rm CF_3Br$ on P6. The coefficient A is in fact, as follows from (2), the dissociation probability of the population of the interval ΔE. For $^{13}\rm CF_3Br$ on the P24 line the MPD quantum efficiency is $\varphi \lesssim 1$, meaning that the molecules dissociate from ΔE with a probability close to 1. It was this condition that led to the choice of the interval 100–150 $\rm cm^{-1}$. For $^{13}\rm CF_3Br$ excited at the center of the nonlinear-absorption band (the P6 line) the interval ΔE was expanded to $\sim 200\ \rm cm^{-1}$. It contained the first two energy levels of the modes $\nu_5 = 545\ \rm cm^{-1}$ and $\nu_3 = 351\ \rm cm^{-1}$. The probability of dissociation from these states was assumed for simplicity to be the same, $A = 5.2 \cdot 10^{-2}$. At average starting energies 700–810 $\rm cm^{-1}$ (see Table I) the interval ΔE contains the energy levels $\nu_6 + \nu_3 = 654\ \rm cm^{-1}$, $2_{\nu 3} = 705\ \rm cm^{-1}$, $\nu_2 = 762\ \rm cm^{-1}$, $\nu_6 + \nu_5 = 850\ \rm cm^{-1}$.

TABLE I. Starting vibrational energies $E_{\rm vib}$ for MPD of $\rm CF_3Br$.

Laser line	$E_{\rm vib}$, $\rm cm^{-1}$	
	$^{13}\rm CF_3Br$	$^{12}\rm CF_3Br$
9P6	450	700
9P18	760	2200/990
9P24	810	2500/750

If molecules are excited from two intervals with different average energies ($^{12}\rm CF_3Br$ on P18 and P24) the MPD yield can be expressed in the linear approximation as $^{12}\beta = A_1\Delta N(E_1) + A_2\Delta N(E_2)$, assuming that $\Delta E_1 = \Delta E_2 = 100 - 150\ \rm cm^{-1}$. In this expression $\Delta N(E_1)$ and $\Delta N(E_2)$ are the equilibrium vibrational-state populations in different intervals having average energies E_1 and E_2, while A_1 and A_2 are the corresponding dissociation probabilities. The relation

$$\ln\{[A_1\Delta N(E_1) + A_2\Delta N(E_2)]Z_{\text{кол}}\} = f(T^{-1})$$

agrees well with the experimental points if we use the following values for the probabilities: $A_1 = 0.9$, $A_2 = 3.0 \cdot 10^{-3}$ for P24 and $A_1 = 0.8$, $A_2 = 9.0 \cdot 10^{-3}$ for P18.

Since A_1 and A_2 differ by two orders of magnitude, it can be concluded that for MPD on the far long-wave edge of the linear-absorption band the field dissociates molecules simultaneously from two energy intervals, but with substantially different probabilities. Figure 3 illustrates the variation of the molecules' starting energy $E_{\rm vib}$ with increasing detuning $\Delta\omega_{\rm las}$. When excited at the center of the linear absorption band ($\Delta\omega_{\rm las} = -0.5\ \rm cm^{-1}$) the molecules dissociate from states ν_3 and ν_5 with average energy 450 $\rm cm^{-1}$, in which case the dissociation probability is low ($A = 5.2 \cdot 10^{-2}$). With increasing detuning, the radiation effectively ($A \approx 0.8$) dissociates molecules with starting energies 750–810 $\rm cm^{-1}$. As the detuning increases further, the probability of dissociation from this level group decreases ($\mathrm{A} \approx (3\text{–}9) \cdot 10^{-3}$) and the field begins to effectively ($A \approx 0.8\text{–}0.9$) excite low-lying states with $\mathrm{E_{vib}} < 2000\ \rm cm^{-1}$, which make the main contribution to the MPD yield of $^{12}\rm CF_3Br$ at $T > 250$ K.

The known increase of the MPD isotopic selectivity as the long-wave detuning is increased and as the gas temperature is lowered, which has been observed for many molecules, now acquires a clear physical meaning.

In fact, in MPD of $\rm CF_3Br$ the dissociation yields of $^{12}\rm CF_3Br$ and $^{13}\rm CF_3Br$ on the P18 and P24 lines at room temperature are determined by molecules that start with appreciably different initial energies. These are $\sim 760\text{–}810\ \rm cm^{-1}$ for the resonant $^{13}\rm CF_3Br$ molecule and 2200–2500 $\rm cm^{-1}$ for the nonresonant $^{13}\rm CF_3Br$. As the temperature is lowered, the populations of the higher states "freeze out" more effectively so that the dissociation yield $^{12}\beta$ of the nonresonant isotope decreases more rapidly than that of the resonant one (see Fig. 1a). As a result, when the gas is cooled the dissociation selectivity increases.

We note, however, that under certain conditions an inverse situation can be observed, where lowering the temperature decreases the selectivity. This occurs if the starting-state energies of the molecules with the desired isotope exceeds those of the molecules with the other isotope. This situation

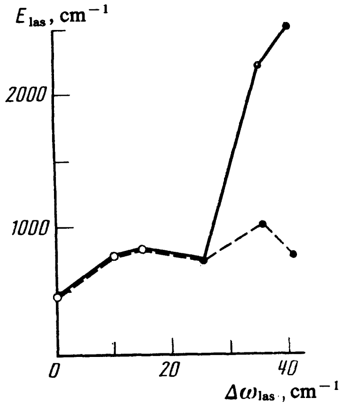

FIG. 3. Starting energy E_{vib} of molecules versus the detuning $\Delta\omega_{las}$ of the exciting-radiation frequency from the center of band ν_1 of the linear absorption: ○—$^{13}CF_3Br$, ●—$^{12}CF_3Br$. Solid line—$T > 250$ K; dashed—$T < 250$ K.

is possible, in particular, for "blue" detuning from both isotopes. It is probably this mechanism which is responsible for the decrease, observed in Ref. 12, of the MPD selectivity of CF_2Cl_2 with decreasing temperature.

The reason why the MPD selectivity increases when the radiation frequency is shifted towards the red is that at $T > 250$ K the starting energy begins to increase when the detuning satisfies $\Delta\omega_{las} > 26$ cm^{-1} (see Fig. 3) This degree of detuning is realized primarily for a nonresonant molecule $^{12}CF_3Br$, for which the radiation frequency had already been displaced to the long-wave region by an amount equal to the isotope shift. Consequently, when the frequency is detuned from the band center of the resonant molecule $^{13}CF_3Br$ the nonresonant-isotope dissociation yield begins to be determined by ever higher vibrational states. The population of these states decreases with increasing energy, meaning that the $^{12}CF_3Br$ MPD yield decreases. At the same time, since the $^{13}CF_3Br$ dissociation probability increases (A increases from $5.2 \cdot 10^{-2}$ to 0.8 when the frequency is shifted by 15.8 cm^{-1}, the MPD yield increases and reaches a maximum. As a result, the MPD selectivity $\alpha = {}^{13}\beta / {}^{12}\beta$ increases with increasing detuning towards longer wavelengths.

We note in conclusion that the described mechanism of formation of the selectivity and its frequency and temperature dependences is applicable to a large class of molecules with small q-factors.

We consider now the size of the energy interval ΔE. We chose it to reconcile numerically the fraction of molecules in the interval and the dissociation yield. The coefficients A, or in fact the dissociation probabilities, are close to unity in certain cases. This is equivalent to stating that the field causes dissociation of almost the entire rotational distribution ($A \sim 1$) of the resonant vibrational levels, which make at $T > 250$ K the main contribution to the MPD yield. It was already noted earlier, however, that the MPD yield for CF_3Br can be increased by adding a buffer gas,[11] a fact attributed to overcoming the rotational "bottleneck." Allowance for this fact may require expanding the band to 300–400 cm^{-1}. It is possible, however, that the main contribution to the increased yield is made by accelerating the rotational relaxation by the nonresonant ($A \sim 10^{-3}$) vibrational levels, in which case the width of the ΔE interval remains unchanged.

As for states with $E_{vib} > 2000$ cm^{-1}, it is quite probable that in this case the fields no longer interact with a level band, but instead with the entire "tail" of the vibrational distribution, except that the molecule-dissociation probability is decreased accordingly. Calculations do not offer a way of choosing between these two possibilities.

We turn now once more to the ratio of the initial vibrational and rotational energies of the molecules drawn into the MPD. On the basis of the data of Ref. 11, we have assumed as the first step that the rotational energy of the dissociating molecules approximately equals its average value, and have thus taken it out of consideration and assumed that the vibrations have the energies given by Eq. (4).

We consider now another limiting case. Assume that the field dissociates the molecules from the rotational distribution of the vibrational ground state. The starting energies obtained from (3) are then purely rotational. Numerical calculation yielded the temperature dependence of the equilibrium population of the rotational states in the energy interval $\Delta E = 100$–150 cm^{-1}, with a mean value equal to the starting one. The calculation results differ qualitatively and quantitatively from the experimental ones in this case.

First, the populations of both the interval and the tail of the rotational distribution cannot account for the dissociation yields observed on the P 18 and P 24 lines for $^{13}CF_3Br$ in the entire temperature range, and for $^{12}CF_3Br$ at $T > 250$ K.

Second, if the molecules come from two energy intervals (as is observed for $^{12}CF_3Br$ on the lines P 18 and P 24), it is impossible to obtain a dependence

$$\ln[A\Delta N(E) Z_{vib} Z_{rot}] = f(T^{-1}),$$

that is qualitatively similar to the experimental one,

$$\ln({}^{12}\beta Z_{vib} Z_{rot}) = f(T^{-1}),$$

by using only the rotational distribution of the vibrational ground state.

Thus, the purely rotational distribution of the ground vibrational state explains the observed dissociation yields and their temperature dependences neither qualitatively nor quantitatively. This result is one more argument in favor of the earlier assumption concerning the ratio of the vibrational and rotational components of initial energy of the molecules drawn into the MPE process.

5. CONCLUSIONS

The experiments show that the initial energies of dissociated molecules can indeed be determined from the temperature dependence of the MPD yields. By using additional data[11] to estimate the rotational energy one can separate the vibrational and rotational components of the initial energy and thus determine the starting vibrational energy of the molecules.

The results have shown that at small levels of frequency detuning, towards longer wavelengths, of the radiation frequency from the center of the linear absorption band ($\Delta\omega_{las} = -0.5$–$15.3$ cm^{-1}) the major contribution to the formation of the hot ensemble is made by states with initial vibrational energy 450–810 cm^{-1}. The dissociation probability increases in this case as the detuning increases.

With further increase of the frequency shift ($\Delta\omega_{\mathrm{las}} = 26.2$–$41.5\ \mathrm{cm}^{-1}$) the probability of dissociation from this group of levels decreases (to $\sim 10^{-3}$). The field begins to excite effectively ($A \approx 0.8$–0.9) the high-lying vibrational states having $E = 2200$–$2500\ \mathrm{cm}^{-1}$, which at $T > 250$ K make the main contribution to the q-factor, and hence to the MPD yield.

When an isotope mixture ($^{12}CF_3Br$ and $^{13}CF_3Br$) is excited, the MPD yields (at $T > 250$ K) are determined for each isotope by level bands with substantially different initial vibrational energy. It is this which determines the observed temperature and frequency dependences of the MPD selectivity.

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[1]E. P. Velikhov, V. Yu. Baranov, V. S. Letokhov, E. A. Ryabov, and A. N. Starostin, Pulsed CO^2 Lasers and Their Use for Isotope Separation [in Russian], Nauka, 1983, No. 5.2.2, 6.1
[2]S. S. Alimpiev, V. N. Bagratashvili, N. V. Karlov, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **25**, 582 (1977) [JETP Lett. **25**, 347 (1977).
[3]J. A. O'Neill and J. R. Robins, J. Chem. Phys. **81**, 1825 (1984).
[4]V. N. Bagratashvili, V. S. Dolzhikov, V. S. Letokhov, and E. A. Ryabov, Pis'ma Zh. Tekh. Fiz. **4**, 1181 (1978) [Sov. J. Tech. Phys. Lett. **4**, 475 (1978)].
[5]M. Droin, M. Gauthier, R. Pilon, P. A. Hackett, and C. Willis, Chem. Phys. Lett. **60**, 16 (1978).
[6]T. F. Deutsch, Opt. Lett. **1**, 25 (1977).
[7]J. L. Lyman, R. G. Anderson, R. A. Fisher, and B. J. Feldman, Opt. Lett. **3**, 238 (1978).
[8]P. A. Hackett, M. Gauthier, C. Willis, and R. Pilon, J. Chem. Phys. **71**, 546 (1979).
[9]W. Tsay, C. Riley, and D. O. Ham. *ibid* **70**, 3558 (1979).
[10]V. P. Zharov, V. S. Letakhov, and E. A. Ryabov, Appl. Phys. **12**, 15 (1977).
[11]O. N. Avatkov, V. B. Laptev, E. Ya. Ryabov, and N. P. Furzikov, Kvant. Elektron. (Moscow) **12**, 576 (1985) [Sov. J. Quant. Electron. **15**, 375 (1985).
[12]J. S. J. Chen and E. R. Grant, J. Chem. Phys. **74**, 5679 (1981).

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