

Vibrational distribution produced by infrared multiphoton excitation of CF_2HCl molecules

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An experimental study has been carried out of the infrared multiphoton excitation (MPE) of CF_2HCl molecules in the two-frequency field of a CO_2 laser. It has been found that this molecule exhibits features that are substantially different from those of molecules studied previously. When CF_2HCl is subjected to MPE in a single-frequency field, the molecules are found to “stick” in the lower discrete state and only a relatively small fraction of them is excited to the vibrational quasicontinuum even in the presence of strong rotational relaxation. It is shown that, under these conditions, the two-frequency laser field can excite a large fraction of the molecules to the vibrational quasicontinuum for moderate laser power densities ($\Phi_1 \approx \Phi_2 \lesssim 2 \text{ J/cm}^2$). A simple model providing a good description of experimental results is considered. Important consequences of the sticking effect are discussed: (1) the usual estimate of the fraction of molecules excited to the quasicontinuum, based on the comparison of dissociation yield or absorbed energy under collisionless and collisional conditions, is invalid and (2) there is a substantial increase in selective MPE yield of the CF_2HCl molecules in the two-frequency laser field.

1. INTRODUCTION

One of the main problems that arise in the study of multiphoton excitation of molecules by infrared laser radiation is the evolution of the vibrational energy distribution during the excitation process.¹ Early advances in the theoretical description of excitation of low-lying vibrational states (the vibrational quasicontinuum, VQ) had already led to calculations of the distribution over the VQ vibrational states within the framework of the rate equations.^{2,3} However, the distribution obtained as a result of this approach could not be used to relate the observed dissociation yield to the measured absorbed energy.⁴

An important step toward an understanding of the infrared excitation of molecules was the observation, for example in OsO_4 , of two groups formed during infrared multiphoton excitation, namely, a “hot” group corresponding to molecules excited to the VQ and a “cold” group consisting of unexcited molecules.⁵ The hot group was characterized by the fraction f of molecules it contained and their average energy,^{6,7} and a number of simple methods were proposed^{6,8} for the experimental determination of these quantities. The two ensembles were subsequently detected by probing vibrationally-excited SF_6 molecules with continuous CO_2 -laser radiation, and the fraction of excited molecules was measured.⁹ A clear confirmation of the existence of these two groups was provided by experiments on the probing of vibrationally excited SF_6 molecules by spontaneous Raman scattering.¹⁰

The concept of the two groups has led to a reconciliation of dissociation yield and absorbed energy data.^{11,12} However, the evolution of the vibrational distribution over the lower discrete vibrational states has so far remained an open question. This problem is particularly relevant for molecules with a high VQ limit and, consequently, an extensive net of discrete levels. The existence of a distribution over the

discrete levels was indicated by experiments on the emission of infrared luminescence by vibrationally excited SF_6 molecules.¹³ Experiments using coherent anti-Stokes Raman scattering (CARS) have enabled direct observations to be carried out of the distribution over the lower discrete states during the excitation of a cooled SF_6 gas by CO_2 laser radiation.¹⁴

In this paper, we consider a reasonably general mechanism for the evolution of an ensemble of molecules occupying the lower discrete states, which relies on reduction in the rate of induced transitions at a particular stage of excitation. It will be shown that this reduction may lead to the “sticking” of the molecules in discrete states even under conditions of strong rotational relaxation. The reason for the reduction in the rate of stimulated transitions may be, for example, the departure of a molecule from resonance as the lower levels are traversed.¹⁵

The basic idea underlying our experimental investigation of molecules distributed over the lower discrete states was to excite successively the “sticking” molecules to the VQ, and to follow this by dissociation by multifrequency infrared laser fields tuned to the successive transitions within the net of discrete levels. Molecules occupying the lower levels are detected by comparing single- and two-frequency excitation of the CF_2HCl molecules which have a relatively high VQ limit. The second field is used simultaneously both for the optimum excitation of molecules distributed over the lower vibrational states to the VQ and to dissociate molecules in the VQ with probability close to unity.

We shall show that, when CF_2HCl is excited by an infrared laser field of moderate intensity, the main ensemble consists of molecules distributed over the lower discrete states. A relatively small fraction of molecules is excited to the VQ and forms the hot ensemble. The observed sticking imposes an essential limitation on the validity of the usual estimates of f (Refs. 8 and 16–18) and explains the apparent

paradoxical lack of increase in f with increasing laser intensity in the case of the CF_2HCl molecule.¹⁶

Section 2 describes the experimental method and conditions. The experimental results are given in Sec. 3. Section 4 presents a qualitative explanation of these results and a simple model. Possible applications of the sticking effect are discussed in the concluding section.

2. EXPERIMENT

Molecules distributed over the lower discrete states were examined by successively dissociating the sticking molecules by radiation from a second CO_2 -laser. Pulsed tunable CO_2 lasers with transverse discharges were used in the experiment. The radiation pulse of frequency Ω_1 , produced by the first laser, had the usual shape: the peak was 75 ns long (150 ns in Fig. 1) and the tail 500 ns long (at half height). Radiation from the second laser of frequency Ω_2 consisted of a 100-ns peak and a 1- μs tail (at half height). The pulses were synchronized to within ± 50 ns.

Both lasers produced multimode radiation. The transverse radiation-density distribution was determined by scanning the beams with a 0.5-mm diameter diaphragm in horizontal and vertical directions. The corresponding radii were determined at the $1/e$ level. The influence of spatial effects due to the transverse distribution of energy in the laser beams on the observed functions $F_m(\Phi)$ was estimated on the assumption that the radial distribution was Gaussian, i.e., $E(r) = E_0 \exp(-r^2/r_0^2)$, using the well-known relation¹⁹

$$F_r(\Phi) = F_m(\Phi) \frac{d[\ln F_m(\Phi)]}{d(\ln \Phi)}, \quad (1)$$

where $F_r(\Phi)$ is a certain function of the energy density corresponding to a homogeneous spatial distribution of energy density, corresponding to a uniform spatial distribution of radius r_0 .

The experiment was performed at moderate laser energy densities $\Phi_{1,2} = (1-4) \text{ J/cm}^2$. The laser radiation was collimated by NaCl lenses (focal length 1 m) and was directed onto an aluminium cell (120 mm long, 12 mm in diameter) with NaCl windows. The two beams propagated in opposite directions at a small angle to each other.

The dissociation yield β per laser pulse was determined spectrophotometrically by measuring the infrared absorption coefficient at 115 cm^{-1} (the ν_8 mode), using the relation

$$k = k_0(1 - \beta V^*/V)^n, \quad (2)$$

where k_0 , k are, respectively, the absorption coefficients at the ν_8 maximum before and after illumination, V , V^* are the total and illuminated volumes of the cell, respectively, and n is the number of illuminating pulses. The monomolecular decay of the SF_2HCl molecule is well-known.^{16,18,20} Under excitation by the CO_2 laser radiation, the CF_2HCl molecule dissociates into the fragments CF_2 and HCl . The dissociation energy is $18 \times 10^3 - 20 \times 10^3 \text{ cm}^{-1}$ (Ref. 20). Recombination of the CF_2 radicals proceeds at the constant rate of $2.2 \times 10^{10} \text{ cm}^{-1}/\text{mole}$ (Ref. 21) and results in the formation of the C_2F_4 molecule.

The most complete review of the spectroscopic characteristics of the CF_2HCl molecule (point group C_s) is given in

Ref. 22 in which a study was made of the infrared absorption spectrum of CF_2HCl gas dissolved in liquid argon at 100 K. The CO_2 laser generation region is overlapped by two modes, namely, $\nu_8 = 1115 \text{ cm}^{-1}$ and $\nu_3 = 1100 \text{ cm}^{-1}$. The estimated ν_8 , ν_3 intramode anharmonic constants based on the first overtone frequencies obtained in Ref. 22 yield $X_{88} = -3.5 \text{ cm}^{-1}$, $X_{33} = -5 \text{ cm}^{-1}$. The rotational constants of the CF_2HCl molecule are: $A_0 = 0.341 \text{ cm}^{-1}$, $B_0 = 0.160 \text{ cm}^{-1}$, $C_0 = 0.116 \text{ cm}^{-1}$ (Ref. 23).

3. EXPERIMENTAL RESULTS

A. Comparison of single- and two-frequency excitation

Figure 1 presents the dissociation yield as a function of the buffer gas (Xe) pressure during the excitation of the CF_2HCl molecule by single-frequency infrared laser fields of frequency $\Omega = 1084.6 \text{ cm}^{-1}$, $9R(30)$ and energy density $\Phi = 1.8 \text{ J/cm}^2$ (curve 1). The upper graph (curve 2) shows the corresponding result obtained under two-frequency excitation with $\Omega_1 = 1084.6 \text{ cm}^{-1}$, $9R(30)$ and $\Omega_2 = 1053.9 \text{ cm}^{-1}$, $9P(12)$, using energy densities $\Phi_1 = 1.8$ and $\Phi_2 = 1.5 \text{ J/cm}^2$, respectively. The CF_2HCl gas pressure in the cell was 0.5 Torr.

Both curves (curves 1 and 2) consist of an initial increasing segment, followed by a practically horizontal portion on which the yield is almost independent of the buffer-gas pressure (in the pressure range under investigation). The rise in the dissociation yield over the initial segment is much greater under two-frequency excitation, which means that the addition of the second field frequency Ω_2 can be used

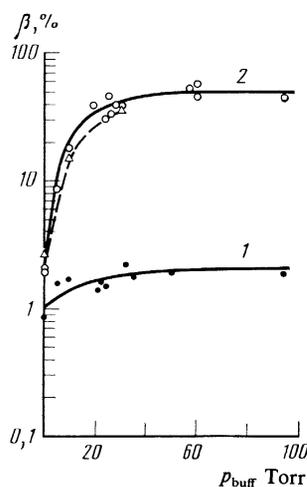


FIG. 1. Dissociation yield of CF_2HCl molecules as a function of buffer-gas pressure (Xe) for single-frequency $\beta_1(P_{\text{buff}})$ (●) and two-frequency $\beta_2(P_{\text{buff}})$ (○) excitation. Solid curves represent the theoretical results deduced on the basis of our model. Broken curves and triangles show the possible effect of the spatial energy density distribution $E_1(r)$ on the nature of the function $\beta_2(P_{\text{buff}})$ when $E_1(r)$ is assumed to be Gaussian. The transition to the uniform radial distribution was performed in accordance with (1). Single-frequency excitation was carried out at the frequency $\Omega = 1084.6 \text{ cm}^{-1}$ with energy density $\Phi = 1.8 \text{ J/cm}^2$. Two-frequency excitation was performed at the frequency $\Omega = 1084.6 \text{ cm}^{-1}$ with energy density $\Phi = 1.8 \text{ J/cm}^2$. In the case of two-frequency excitation, $\Omega_1 = 1084.6 \text{ cm}^{-1}$, $\Omega_2 = 1053.9 \text{ cm}^{-1}$; $\Phi_1 = 1.8 \text{ J/cm}^2$, $\Phi_2 = 1.5 \text{ J/cm}^2$. The delay between the pulses was $\Delta\tau = 600 \pm 50$ ns. The laser pulse length at the frequency Ω_1 was: peak 150 ns, tail 500 ns (at half height). The CF_2HCl gas pressure in the cell was 0.5 Torr.

under strong rotational relaxation to produce additional trapping of molecules from certain intermediate states, the depletion of which is impossible under single-frequency excitation.

In the ensuing discussion, we shall characterize the influence of the buffer gas on the dissociation yield by the ratio φ of dissociation yields at zero buffer-gas pressure $\beta(0)$ and at the pressure P_{sat} corresponding to the onset of the horizontal portion of the curve (Fig. 1). Previously, under single-frequency excitation, φ_1 was identified with the fraction $f(0)$ of molecules excited to VQ under collisionless conditions.¹⁶⁻¹⁸ For the single- and two-frequency excitation of CF_2HCl molecules shown in Fig. 1, we have $\varphi_1 = 0.5$, $\varphi_2 = 0.08$.

For single-frequency excitation with $\Omega = 1084.6 \text{ cm}^{-1}$, the ratio $\varphi_1 = \beta_1(0)/\beta_1(P_{\text{sat}})$ falls slowly with increasing laser energy density in the range $2-5 \text{ J/cm}^2$. Actually, $\varphi_1 = 0.5 \pm 0.05$ for $\Phi = 2 \text{ J/cm}^2$ and $\varphi_1 = 0.4 \pm 0.05$ for $\Phi = 5 \text{ J/cm}^2$. A similar variation in $\varphi_1(\Phi)$ for the CF_2HCl molecule in the energy-density range $2-9 \text{ J/cm}^2$ can be obtained from an analysis of the data reported in Ref. 16. In both cases, φ_1 does not increase with increasing energy density. It is important to emphasize that this behavior of φ_1 is in conflict with the usual behavior of f as the energy density increases, i.e., as unity is approached.^{9,24} This also indicates that, for the CF_2HCl molecule, the ratio φ_1 cannot be identified with the fraction f of excited molecules.

B. Estimated fraction of molecules excited to the VQ

We used the method developed in Refs. 5 and 7 to estimate the fraction of molecules excited to the VQ by laser radiation. This method is based on the principle that molecules reaching the VQ will dissociate with probability close to unity under the influence of laser radiation of frequency Ω_2 , which is the optimum frequency for traversing the quasi-continuum. If this is so, and if we assume that the second field does not influence molecules distributed over the states below the VQ limit, the dissociation yield gives directly the fraction of molecules excited by the first field into the quasi-continuum. In practice, owing to the partial trapping by the second field of molecules distributed over the discrete vibrational states, the dissociation yield obtained in this way serves as the upper limit for the fraction f .

Figure 2a shows the dissociation yield as a function of the energy density of the second laser field. The energy density Φ_1 of the first field was held constant at 2 J/cm^2 . The lower curve was obtained for CF_2HCl gas pressure in the cell equal to 0.5 Torr. The upper curve corresponds to the excitation of a mixture of 0.5 Torr of CF_2HCl and 32 Torr of Ar. The frequencies of the first and second laser fields were 1084.6 cm^{-1} , $9R(30)$ and 1053.9 cm^{-1} , $9P(12)$, respectively. In the absence of the buffer gas, it is clear from Fig. 2a that, in the range $1.3-3 \text{ J/cm}^2$, the dissociation yield is a slowly-varying function of the energy density produced by the second laser field: $\beta_2 \propto \Phi_2^{0.5}$, i.e., the second field dissociates molecules reaching the VQ with probability close to unity. It follows from Fig. 2a (lower curve) that, when $\Phi_1 = 2 \text{ J/cm}^2$, the fraction of such molecules is $f < 0.06$.

As the energy density increases ($\Phi_2 \gtrsim 3 \text{ J/cm}^2$), we ob-

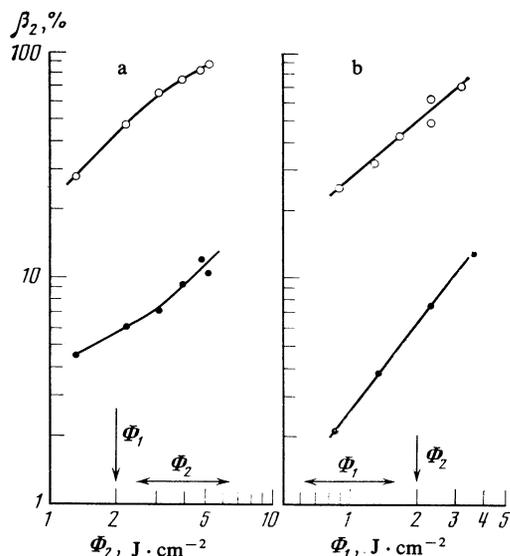


FIG. 2. Dissociation yield as a function of laser radiation density for two-frequency excitation of CF_2HCl molecules at constant Φ_1 (a) and Φ_2 (b): lower curves were obtained for CF_2HCl pressure of 0.5 Torr and the upper curves for 0.5 Torr of CF_2HCl and 32 Torr of Ar. The energy density was $\Phi_1 = 2.0 \text{ J/cm}^2$ (a) and $\Phi_2 = 2.0 \text{ J/cm}^2$ (b). The delay between the pulses was $\Delta\tau = 600 \pm 50 \text{ ns}$.

serve a more rapid rise in dissociation yield ($\beta_2 \propto \Phi_2$) (lower curve in Fig. 2a). This probably means that, when the higher energy density is reached ($\Phi_2 \gtrsim 3 \text{ J/cm}^2$), the second field produces more effective excitation of molecules from the lower discrete levels. This effect is enhanced when the buffer gas is added, i.e., capture from the discrete-level net begins at lower energy densities. This can be seen in the more rapid variation of the dissociation yield with the energy density of the second field: $\beta_2 \propto \Phi_2$ ($1.3 \text{ J/cm}^2 \lesssim \Phi_2 \lesssim 3 \text{ J/cm}^2$) (upper curve in Fig. 2a). This curve tends to saturate as the energy density is increased still further.

Figure 2b shows the dissociation yield as a function of the energy density of the first laser field, where the parameters of the second field ensure saturation of the VQ, i.e., the probability of dissociation of a molecule entering the quasi-continuum is close to unity. The lower curve corresponds to the two-frequency excitation of CF_2HCl (0.5 Torr) and the upper to the excitation of a mixture of CF_2HCl (0.5 Torr) and Ar (32 Torr). In the absence of the buffer gas, the dissociation yield is a relatively rapidly-varying function of the energy density of the first field: $\beta_2 \propto \Phi_1^{1.3}$ in the density range $0.9-3.7 \text{ J/cm}^2$. When the buffer gas is added (upper curve in Fig. 2b), this variation becomes slower: $\beta_2 \propto \Phi_1^{0.9}$. These relations provide us with an estimate for the upper limit of the fraction of molecules excited by the first field into the VQ under near-collisionless conditions (lower curves) and in the presence of rapid rotational relaxation by collisions with buffer gas molecules (upper curve).

Comparison of the value of f with the quantities φ_1 , φ_2 in the case of single- and two-frequency excitation ($\varphi_1 = 0.5$ and $\varphi_2 = 0.08$) leads to the following conclusions: (1) an ensemble of molecules distributed over the lower discrete levels is formed under single-frequency excitation of CF_2HCl

molecules both under near-collisionless conditions and under strong rotational relaxation; only a small fraction of molecules [$f(0) < 0.06$ in the collisionless regime of excitation and $f(P_{\text{sat}}) = f(0)/\varphi_1 < 0.12$ under strong rotational relaxation] enters the VQ under the corresponding conditions of single-frequency excitation and (2) $f(P_{\text{sat}})$ does not reach unity even under two-frequency excitation in the presence of strong vibrational relaxation, i.e., some of the molecules remain in discrete states ($f(P_{\text{sat}}) = f(0)/\varphi_2 < 0.75$).

C. Relaxation to intermediate states

It is clear from Fig. 1 that collisional relaxation processes leading to a rapid rise in the yield are important in the two-frequency experiment. Two basic factors can determine this type of pressure dependence of β_2 . Firstly, the molecules excited by the first field in a nonequilibrium manner can relax during the interval $\Delta\tau$ between pulses to vibrational-rotational levels from which they can be effectively removed to the VQ by a field of frequency Ω_2 . Secondly, discrete levels depleted by the second field may become occupied as a result of rotational relaxation during the time of the second pulse, i.e., an increase in the buffer-gas pressure can overcome the "rotational bottleneck" involving excited states below the VQ. These two mechanisms should cause the delay between the first and second laser pulses to have qualitatively different effects on the dissociation yield. Actually, in the first case, as the delay $\Delta\tau$ increases, we should observe the same rapid rise in the dissociation yield as when the buffer-gas pressure P_{buff} is increased (Fig. 1). In the second case, collisional excitation of the molecules should occur during the second laser pulse τ_2 and, consequently, the dissociation yield should be independent of $\Delta\tau$.

We have investigated the dissociation yield as a function of the delay between the two exciting laser pulses for the following laser radiation parameters: $\Omega_1 = 1084.6 \text{ cm}^{-1}$, $9R(30)$; $\Omega_2 = 1055.6 \text{ cm}^{-1}$, $9P(10)$; $\Phi_1 = \Phi_2 = 2 \text{ J/cm}^2$. We considered two cases, namely, (1) zero buffer-gas pressure and (2) 32 Torr of added argon, i.e., essentially collisional excitation. In both cases, the quantity β_2 was found to rise by a factor of only 1.5 when the delay $\Delta\tau$ was increased from 0 to $1 \mu\text{s}$. The observed behavior of $\beta_2(\Delta\tau)$ shows that the second mechanism, which relies on rotational relaxation during the second pulse, probably exerts the main influence on the collisional increase in the dissociation yield under two-frequency excitation.

For long delays (1–3.5 μs) and zero buffer-gas pressures,

the dissociation yield is practically constant. Under collisional excitation, the dissociation yield falls in this delay range by a factor of about two because of deactivation of molecules excited by the first pulse as a result of V - T relaxation.

D. Frequency characteristics

Figures 3a and b show the dissociation yield as a function of the second laser frequency Ω_2 when the gas pressure in the cell was 0.5 Torr (Fig. 3a) and when 32 Torr of the buffer gas (Ar) was added (Fig. 3b). The frequency of the first field was held constant at $\Omega_1 = 1084.6 \text{ cm}^{-1}$, $9R(30)$. Under near-collisionless excitation (Fig. 3a) at the frequency of 1075 cm^{-1} , we observed a relatively narrow peak whose width was comparable with the width of the Q branch of the ν_8 mode in the linear infrared absorption spectrum of CF_2HCl . Under collisional excitation (Fig. 3b), we observed a rapid increase in the long-wave wing at frequencies below 1060 cm^{-1} .

The observed structure of the dissociation spectrum $\beta_2(\Omega_2)$ is probably due to resonances on the discrete net of vibrational states. The ν_3 mode, which is the closest to the observed resonance at 1075 cm^{-1} , has the anharmonic constant $X_{33} = -5 \text{ cm}^{-1}$ (Ref. 22). If the observed resonance was due to this mode, it may have been associated with the Q branch corresponding to $3 \leftarrow 2$ or $4 \leftarrow 3$ transitions in the ν_3 mode. A more precise identification will require precise knowledge of the spectroscopic constants of CF_2HCl molecules.

4. QUALITATIVE CONSEQUENCES AND MODEL

We now turn to a simple model for the lifting of the molecules into the VQ (Ref. 25), which will enable us to obtain a qualitative explanation of the evolution of the energy distribution of the molecules and the fact that "sticking" cannot be overcome under single-frequency excitation even when the conditions of strong rotational relaxation obtain.

Let us now suppose that only a certain fraction q of the molecules interacts effectively with the field. For example, these can be the molecules occupying rotational sublevels that are in resonance with the field. If the rate of excitation to the VQ is W , we have, under near-collisionless conditions,

$$f(0) = q[1 - \exp(-W\tau)], \quad \beta(0) = f(0)\alpha_{\text{VQ}}, \quad (3)$$

where α_{VQ} determines the rate at which the molecules leave the VQ through dissociation and τ is the laser pulse length.

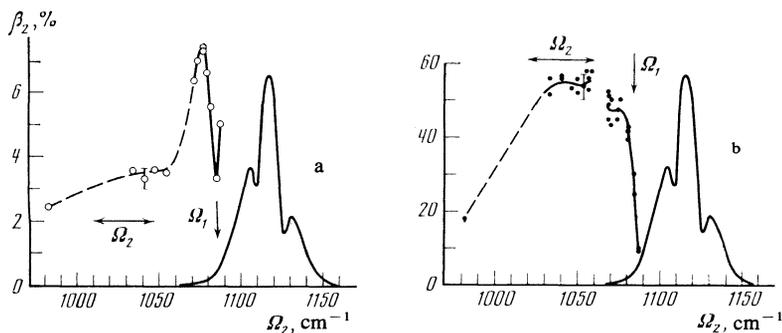


FIG. 3. Dissociation yield β_2 as a function of the frequency Ω_2 of the second laser without (a) and with (b) the buffer gas. The energy density was $\Phi_1 = 2.0 \text{ J/cm}^2$, $\Phi_2 = 1.6 \text{ J/cm}^2$. The delay was $\Delta\tau = 600 \pm 50 \text{ ns}$. For comparison, we show the linear infrared absorption band of the CF_2HCl molecule.²²

When the pressure is high enough, a quasistationary distribution is established over the vibrational states, and the rate of excitation of all the molecules is $W_{\text{eff}} \approx qW$, i.e.,

$$f(P_{\text{sat}}) \approx 1 - \exp(-qW\tau_r), \quad \beta(P_{\text{sat}}) \approx f(P_{\text{sat}})\alpha_{\text{VQ}}. \quad (4)$$

The saturation pressure is then given by the condition $k_{\text{rot}}P_{\text{sat}} \gg W$, where k_{rot} is the rate of rotational relaxation. We thus have

$$\varphi = \frac{\beta(0)}{\beta(P_{\text{sat}})} \approx q \frac{1 - \exp(-W\tau_r)}{1 - \exp(-qW\tau_r)}. \quad (5)$$

Hence, the simple estimate $\varphi \approx q \approx f(0)$ is possible only when $qW\tau_r \gg 1$. When $qW\tau_r \ll 1$, equation (5) does not depend on q at all. It is precisely this that may explain the nonincreasing form of the function $\varphi(\Phi)$.

The above estimate is based on the simple fact that, when the system has several characteristic rates (in our case, radiative excitation and rotational relaxation), the effectiveness of excitation is determined by the lowest of them. Thus, by analogy with the rotational bottleneck, there may also be an "excitation-rate bottleneck" or a "field bottleneck," which means that not all the molecules that can be excited will be excited. Linear absorption ($W\tau_r \ll 1$), for which (5) shows that $\beta(0) = \beta(P_{\text{sat}})$, is an obvious limiting case. We note that the estimate $\varphi \approx df$ (or $\varphi \approx q$ since $f \approx q$ for $W\tau_r \gtrsim 1$) is widely accepted. The above discussion shows, however, that this estimate must be treated with caution and is not valid at all in the case of CF_2HCl molecules.

We can now qualitatively understand the evolution of the ensemble of molecules in discrete states during infrared MPE. Suppose that, as the molecules occupying discrete vibrational levels become excited, the departure from resonance causes a sharp reduction in the rate W of individual excitation, or introduces a field bottleneck. It then follows directly from (5) that, even under essentially collisional conditions (when the buffer gas is added), a substantial fraction of the molecules cannot be excited to the VQ. Excitation in the presence of strong rotational relaxation, on the other hand, effectively populates all the vibrational states lying below the level at which a sharp reduction occurs in the rate of stimulated transitions (Fig. 4a). This excitation results in the preparation of the molecules distributed over the low-lying vibrational states. Only a small fraction of these molecules has a considerable amount of vibrational excitation and constitutes the hot ensemble.

When a second laser field detuned toward the red from the frequency Ω_1 is applied, the anharmonism of the discrete levels can be balanced and the bottleneck thereby removed (Fig. 4b). In this type of excitation, a substantial fraction of the molecules can be taken up into the VQ under conditions of strong rotational relaxation. The main function of rotational relaxation is then to involve the molecules distributed over the rotational sublevels of vibrational states belonging to the discrete net in the process of absorption during the laser pulse of frequency Ω_2 . The model proposed below summarizes these qualitative ideas and provides a satisfactory description of the observed dissociation yields.

The model itself is a generalization of the scheme (Figs. 4a and b) to a two-level system as a way of explaining our

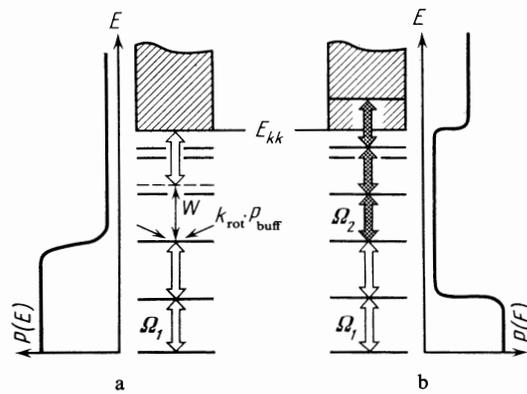


FIG. 4. Illustration of the "sticking" model: qualitative shape of the vibrational distribution $P(E)$ under essentially collisional single-frequency excitation (a) and elimination of sticking under two-frequency excitation (b).

results. Suppose that the lower level A corresponds the situation where all the vibrational states are initially occupied. $N_A(t)$ is its total population. The upper level B represents all the levels below the VQ to which the molecules stick under the influence of the first field. Its population is $N_B(t)$. To simplify the description of the population dynamics, we shall suppose that all the molecules that have been excited from level B undergo dissociation (a more precise treatment of VQ excitation and monomolecular decay does not affect the qualitative results).

The influence of rotational relaxation is taken into account as follows. As an example, consider level A . Its various sublevels interact differently with the incident radiation. The simplest model²⁵ that takes this into account defines two groups of sublevels of A and allows one of them to interact with the radiation. Suppose that $n_a(t)$ is the total population of these resonant sublevels. For the quasistationary distribution (high pressure), we have $n_a = q_a N_A$. We now define W_0 as the rate of excitation from the resonance sublevels of the lower state to some of the sublevels of B . The population of these sublevels of B , which are excited when the field of frequency Ω_1 is turned on, is $n_b(t)$. Let us suppose that the quasistationary population of B is determined by the same q -factor, i.e., $n_b = q_a N_B$.

Next, let us examine the effect of the first field on the level B . In accordance with our assumption, the molecules stick in this level, and this is only partially overcome by rotation relaxation. Since the level B represents a set of vibrational-rotational states lying below the VQ limit in our model, this level must also be subdivided into resonant and nonresonant (with respect to upward excitation) sublevels. With some loss of generality, we shall suppose that the sublevels of B that are in resonance with upward transitions (with rate W_1) are characterized by the q -factor q_b and include both the sublevels with population $n_b(t)$ and some other sublevels with population $n_{b_1}(t)$. It follows that the sublevels n_b receive contributions from below, but are depleted by upward transitions. The sublevels n_{b_1} can at first be excited as a result of rotational relaxation (they receive some of the population n_b) and are then excited upward. In the quasistationary state, $n_{b_1} = (q_b - q_a)N_B$. Here, q_b determines the fraction

of molecules in resonant interaction with the first field during the excitation of level B to the VQ. By simultaneously taking into account both radiative excitation and rotational relaxation, we obtain the following set of rate equations for the interval of time during which the first field is present ($0 \leq t \leq \tau_1$):

$$\begin{aligned} \dot{N}_A &= -W_0 n_a + W_0 n_b, & \dot{n}_a &= -W_0 n_a + W_0 n_b + k_{\text{rot}}^{-1} P (q_a N_A - n_a), \\ \dot{N}_B &= -W_0 n_b + W_0 n_a - W_1 (n_b + n_{b1}), \end{aligned} \quad (6)$$

$$\dot{n}_b = -W_0 n_b + W_0 n_a + k_{\text{rot}}^{-1} P (q_a N_B - n_b) - W_1 n_b,$$

$$\dot{n}_{b1} = k_{\text{rot}}^{-1} P [(q_b - q_a) N_B - n_{b1}] - W_1 n_{b1},$$

$$\beta_1 = \int_0^{\tau_1} W_1 [n_b(t') + n_{b1}(t')] dt'.$$

The initial conditions are

$$N_A(0) = 1, \quad n_a(0) = q_a, \quad N_B(0) = n_b(0) = n_{b1}(0) = 0. \quad (7)$$

When the second field appears, level A is not excited but the molecules leave level B for the VQ (and dissociate) at the rate W_2 :

$$\dot{N}_B = -W_2 n_2, \quad \dot{n}_2 = -W_2 n_2 + k_{\text{rot}}^{-1} P (q_2 N_B - n_2), \quad (8)$$

$$\beta_2 = \int_{\tau_1 + \Delta\tau}^{\tau_1 + \Delta\tau + \tau_2} W_2 n_2(t') dt'.$$

Throughout, $P = P_{\text{CF}_2\text{HCl}} + P_{\text{buflf}}$. In these expressions, n_2 represents the sublevels of B that are in resonance with the second field and from which the molecules are excited at the rate W_2 . The initial conditions for $t = \tau_1 + \Delta\tau$ will be formulated by neglecting V - T relaxation and assuming that the thermal distribution is established over the vibrational sublevels in a time $\Delta\tau$ ($\Delta\tau \approx 0.5$). We have shown experimentally that the yield was a slowly-varying function of the delay $\Delta\tau$.

Thus,

$$N_B(\tau_1 + \Delta\tau) = N_B(\tau_1), \quad n_2(\tau_1 + \Delta\tau) = q_2 N_B(\tau_1). \quad (9)$$

We must now consider the parameters in (6)–(9). The order of magnitude of the rotational relaxation constant is well known: $k_{\text{rot}}^{-1} = 100 \text{ ns} \cdot \text{Torr}$ (Ref. 17). The remaining parameters were varied under the following conditions: $W_0 \gg W_1$ (sticking under the influence of the first field); $W_2 \gg W_1$ (removal of the field bottleneck by the second field); $q_2 < 1$, $q_a < q_b < 1$. The calculated curves shown in Fig. 1 are in good agreement with experiment for the following parameter values: $W_0 = 10^9 \text{ s}^{-1}$; $W_1 = 2.7 \times 10^6 \text{ s}^{-1}$; $W_2 = 5 \times 10^8 \text{ s}^{-1}$; $q_a = 0.1$; $q_b = 0.25$, $q_2 = 0.12$. There is little point in detailing the model any further in the absence of adequate spectroscopic data on the CF_2HCl molecule, since this would introduce new parameters that cannot as yet be determined independently either experimentally or theoretically.

5. CONCLUSION

As a first step, the CF_2HCl molecule can be assigned to a class of small molecules characterized by a relatively high VQ limit and, hence, an extensive discrete net of vibrational levels. The process of traversal of the lower levels of such molecules gives rise to a strong dependence of both the ab-

sorbed energy and the dissociation yield on the laser intensity.²⁰ Precisely the influence of this parameter on multiphoton excitation by infrared radiation that can be used conventionally to classify the molecules into small, intermediate, and large. So far, only the last two classes of molecules have undergone intensive investigation. As far as small molecules are concerned, one usually tries to describe MPE and, in particular, the resulting vibrational distribution, by analogy with the other two classes. Naturally, the necessity for surmounting the extensive discrete net of vibrational levels during the MEP process in small molecules should lead to a number of features in the vibrational distribution that is formed as a result.

We have carried out an experimental study of multiphoton dissociation of the CF_2HCl molecule in a two-frequency infrared laser field. In contrast to the usual approach to two-frequency MPE, in which the first field is essentially used to produce excitation from the lower vibrational levels and the second to produce excitation to the VQ, it is now assumed that, for small molecules, the additional effect of the second field should reduce to the excitation of molecules stuck to discrete levels.

As a result, we have found that the dominant effect in the evolution of the vibrational energy distribution during MPE is the sticking of molecules to the lower discrete states. This effect occurs even under conditions of strong rotational relaxation and ensures that, for moderate laser energy densities, only a small fraction of the molecules can be raised to the quasicontinuum under single-frequency excitation. An important consequence of this effect is that the most frequently employed method of determining the fraction of molecules excited to the quasicontinuum^{8,16–18} is not valid.

Another important result is that it is readily possible to eliminate sticking by MPE in multifrequency infrared laser fields, including the two-frequency field. This result is important because the class of small molecules is probably the most promising from the point of view of implementation of the isotopically highly selective infrared multiphoton dissociation.²⁶ The utilization of this process in multifrequency infrared laser fields results in a considerable increase in the yield and selectivity of dissociation at substantially lower laser energy densities.

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