Investigation of vibrationally excited ammonium molecules by the double IR-UV resonance technique

R. V. Ambartsumyan, V. S. Letokhov, G. N. Makarov, and A. A. Puretskil

Institute of Spectroscopy, USSR Academy of Sciences
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A double IR-UV resonance technique is proposed for investigating the kinetics of molecules vibrationally excited by laser radiation. This method was used: 1) to measure the \( V-T \) relaxation time in the \( \text{NH}_3 \) molecule \((1.9 \pm 0.2 \text{nsecatm})\) and also in the mixtures \( \text{NH}_3-\text{Ar} \) \((188 \pm 5 \text{nsecatm})\), \( \text{NH}_3-\text{O}_2 \) \((120 \pm 10 \text{nsecatm})\), \( \text{NH}_3-\text{Xe} \) \((240 \pm 20 \text{nsecatm})\); 2) to measure the fraction of energy transferred to \( ^{15}\text{NH}_3 \) molecules from \( ^{14}\text{NH}_4 \) molecules pumped by radiation from a \( \text{CO}_2 \) laser; 3) to assess the \( V-V \) exchange time in the \( \text{NH}_3 \) molecule.

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1. INTRODUCTION

The transfer of energy to the vibrational, rotational and translational degrees of freedom of a gas is of considerable practical interest for the kinetics of chemical reactions, in various gasdynamic phenomena, in shock tubes, and also for many other nonequilibrium systems. Knowledge of the probabilities of \( V-T \), \( R-T \) and \( V-V \) relaxations is quite necessary for study of the selective effect of laser radiation on matter, in particular for laser separation of isotopes.\(^{[1-6]}\)

A large amount of data on the kinetics of vibrational excitation has been obtained by observation of infrared (IR) luminescence and absorption of molecules excited by IR laser radiation.\(^{[1]}\) In study of the separation of nitrogen isotopes by selective two-step dissociation of ammonia molecules,\(^{[5-6]}\) a method for direct measurement of the population of the vibrational levels of the ammonia molecules from the changes in the ultraviolet (UV) absorption spectrum was developed.\(^{[2]}\) This method can be called the double IR-UV resonance technique. Study of the change in the UV spectrum of a molecule excited by IR laser radiation presents new possibilities for investigation of the kinetics of vibrational excitation of molecules excited by laser radiation.

IR-UV resonance was applied earlier in investigation of the mechanism of filling of the vibrational levels of the \( \text{NH}_3 \) molecule on excitation by continuous and pulsed radiation from a \( \text{CO}_2 \) laser.\(^{[3]}\) Reference was made to the possibility of using this method to study the kinetics of vibrational excitation in the \( \text{NH}_3 \) molecule with high time resolution. However, the power of the pulsed \( \text{CO}_2 \) laser used in these studies did not allow us to measure the time of the vibrational-translational relaxation \((T_{V-T})\) in the \( \text{NH}_3 \) molecule directly.

In the present study\(^{[3]}\) the time \( T_{V-T} \) in the ammonia molecule was measured by the IR-UV resonance technique, and 2) the fraction of energy transferred from \( ^{14}\text{NH}_4 \) molecules to \( ^{15}\text{NH}_3 \) molecules on pumping of \( ^{14}\text{NH}_4 \) by a \( \text{CO}_2 \) laser pulse was measured by the same technique. The problem of the rate of \( V-V \) exchange between ammonia molecules with different isotopes of nitrogen is discussed on the basis of the fraction of transferred quanta.

2. METHOD OF MEASUREMENT AND EXPERIMENTAL APPARATUS

The method used was essentially as follows: under the action of IR laser radiation on the chosen vibrational level of the ground electron state, a change takes place in the population of this level and, as a consequence, there is a change in the intensity distribution in the electron-vibrational spectrum of the molecules investigated.

When \( \text{CO}_2 \) laser radiation acts on a vibrational transition of an ammonia molecule a “new” absorption line appears in the electron-vibrational spectrum of the \( \text{NH}_3 \). This line corresponds to the electron-vibrational transition \((v' = 0; \tilde{A} \rightarrow v' = 1; \tilde{X})\) and has an intensity approximately four times greater than the intensity of the band corresponding to the transition from the zero vibrational level of the ground electron state \( \tilde{X} \).

On filling of higher vibrational levels, new lines appear in the electron-vibrational absorption spectrum of the \( \text{NH}_3 \) molecule, corresponding to transitions from these vibrational levels to the vibrational levels of the first excited electron state \( \tilde{A} \). All these lines are evidently identical to the “hot” absorption bands of the ammonia molecule; however, the intensity distribution in the electron-vibrational absorption spectrum of the \( \text{NH}_3 \) molecule will be essentially new. The intensity distribution of the electron-vibrational progression will be determined by the distribution of the molecules over the vibrational levels of the ground electron state, which, in the case of excitation of the vibrational levels of the molecule by sufficiently powerful laser radiation, will be essentially different from the Boltzmann distribution.

Thus, after carrying out a standardization according to the “hot” absorption bands of the \( \text{NH}_3 \) molecule, for which the populations of the higher levels \((v' = 1, 2, \ldots ; \tilde{X})\) compare well with the observed intensities of these absorption bands (see, for example,\(^{[1]}\)), we can, by measuring the intensities of the absorption bands that develop under the action of IR laser radiation, measure the population of the levels \((v' = 1, 2, \ldots ; \tilde{X})\) of the \( \text{NH}_3 \) molecule directly (see\(^{[4]}\)).

By observing the time variation of the electron-vibrational absorption bands of the \( \text{NH}_3 \) molecule with the excited vibration levels \((v' = 1, 2, \ldots ; \tilde{X})\), one can study the kinetics of molecules excited by laser radiation; in particular, one can measure the time of vibrational-translational relaxation of the vibration \( \nu_2 \).

A diagram of the experimental arrangement is shown in Fig. 1. The apparatus consisted of the following basic elements: a frequency-tunable atmospheric-pressure \( \text{CO}_2 \) laser with transverse discharge, a source of UV radiation, a cell with the investigated ammonia gas, and a recording system.

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The design of the atmospheric-pressure CO₂ laser was similar to that described in [10,11]. The laser cell was filled with a mixture of gases in the ratio CO₂:N₂:He = 1:1:4. The maximum output of radiant energy was achieved in this case. The laser had shaped electrodes (Bruce profile), which made it possible to obtain a uniform distribution of the electric field intensity in the space between the electrodes (the length of the electrodes was 40 cm, width 6 cm, distance between them 2 cm). Ignition electrodes consisting of two thin tungsten wires of diameter 0.08 mm were placed in the median plane between the shaped electrodes.

A set of external mirrors was used in the laser, one of which was a diffraction grating (100 lines/mm)—an echelle grating cut from AMTs alloy. The grating operated in an autocollimating regime, in the first order, with a reflection coefficient of 70%. The radiant energy was extracted from the zeroth order of the grating. This made it possible to tune the frequency of the laser and to obtain generation at different vibrational-rotational transitions of the CO₂ molecule. A spherical metallic second mirror (R = 8 m) was used.

The maximum energy generated was ~1 J at a 1.0 atm pressure of the mixture in the laser cell. An oscillogram of the radiation pulse is shown in Fig. 2. The length of the generated pulse amounted to ~200 nsec at half-height. The pulse duration was measured by means of an uncooled Ge:Au semiconductor crystal (a “photon-drag” detector). The signal from the detector was fed directly to the oscilloscope. The detector had a time resolution no worse than 5 nsec. To record the pulse we used an S8-2 recording oscilloscope (transmission band 7 MHz), which also determined the time resolution of the recording system.

The smooth, prolonged trailing edge made the generated pulse of the laser unsuitable for relaxation measurements. For this latter purpose, we shaped a pulse with a steep trailing edge: on the path of the laser radiation we placed a telescope consisting of two lenses (NaCl). At the focus of the first lens (f = 5 cm), optical breakdown was observed in air. This caused cutoff of the trailing edge of the laser pulse. The pulse amplitude after breakdown was ~0.6–0.8 of its original value. The pulse energy was 100–200 millijoule. Figure 3 shows an oscillogram of the pulse after the optical breakdown. The insufficiently high resolution of the S8-2 oscilloscope did not permit us to observe the actual shape of the pulse. However, it is known that the trailing edge of the truncated pulse lasted ~1 nanosec. Consequently, the actual pulse duration was 30–50 nanosec. The radiated power was ~2 MW.

As a source of UV radiation, we used an IFP-800 flask tube, which was fed from a band of capacitors of capacitance 500 μF charged to a potential of 1 kV. The tube was shielded and the radiation was extracted from it through an aperture of diameter ~0.4 cm. The pulse duration of the UV radiation from the tube amounted to ~500 μsec. The tube was discharged by a block of an SAP self-starting system.

The cell for the investigated gas was made of glass. It had four windows: two, which were of quartz, were for illumination by the UV radiation (the distance between the windows was LUV = 22 mm) and two were of NaCl, for illumination by the laser radiation (LIR = 21 mm). The cell was so made that the laser beam would completely cover the UV beam. The gas that was used was carefully purified by refreezing in liquid nitrogen at T = 77K.

The recording system consisted of an MDR-2 monochromator, an FEU-39 photomultiplier, an infrared

![Diagram of experimental setup](image)
radiation detector, and an S8-2 oscilloscope. The cell was illuminated by the UV and laser radiation in mutually perpendicular directions. The UV and laser pulses were synchronized by triggering the ignition block of the laser and the block igniting the IFP-800 tube from a GS-15 pulse generator. The laser pulse was delayed by 200–250 μsec relative to the start of the UV radiation, in order to operate at the top (plateau) of the UV pulse.

The filling kinetics of the vibrational level \( v'' = 1 \) was investigated on this apparatus under excitation of the ammonia molecule by the pulsed CO\(_2\) laser. The fraction of the vibrational quanta transferred from one isotopic ammonia molecule to another on pumping of one of them by pulsed radiation from the CO\(_2\) laser was also measured.

3. VIBRATIONAL-TRANSLATIONAL RELAXATION

Shape of filling pulses of the level \( v'' = 1 \); \( \Lambda \). Thermal and radiative parts. Figure 2 shows the pulse-wise increase in the UV absorption on the transition \( v' = 0; \Lambda - v'' = 1; \Lambda \) under pulsed CO\(_2\) laser radiation and the lasing pulses at the line \( P(32) \) of the band \( 00^1 \rightarrow 10^0 \). Figure 3 shows similar pulses for the case in which the laser pulse was cut off by formation of a breakdown in the air. We note that the lag of the peak of the incipient UV absorption pulse behind to the peak of the laser pulse is due to the lag of the system recording the UV radiation, which amounted to 90 nsec, while the photon-drag detector was practically inertia-free.

Examining the incipient UV absorption pulse in the \(^{14}\)NH\(_3\) gas, we can distinguish two parts: the peak in the leading part and the tail of the pulse, whose duration amounted to ~800 μsec along the base at 100 Torr of ammonia in the cell.\(^8\) In order to make clear with what the two parts of the absorption pulse are associated, an inert gas was added to the ammonia in the cell. This led to the disappearance of the tail of the UV absorption pulse. Incipient UV absorption pulses in the mixture of ammonia with the ballast gas are shown in Fig. 4. The disappearance of the tail upon addition of the ballast indicates that the tail is of thermal nature.

We can thus distinguish two processes that lead to formation of the UV absorption pulse in the gas under the action of the IR laser radiation: 1) radiative filling of the level \( v' = 1; \Lambda \) and 2) Boltzmann thermalization of the absorbed IR laser radiation, leading to thermal population of the level \( v' = 1; \Lambda \).

Times of \( V-T \) relaxation of the level \( v' = 1; \Lambda \) in the gases \( \text{NH}_3, \text{NH}_3 - \text{Xe}, \text{NH}_3 - \text{O}_2, \) and \( \text{NH}_3 - \text{Ar} \). From measurements of the time dependence of the UV absorption pulse on the transition \( v' = 0; \Lambda - v'' = 1; \Lambda \) after the end of the laser pulse, data could be obtained on the time of the \( V-T \) relaxation. The cut-off pulse of the CO\(_2\) laser (Fig. 3) is ideal for relaxation measurements. The shape of the UV absorption pulse in ammonia at a frequency of 45 250 cm\(^{-1}\) on excitation by the cut-off pulse of the CO\(_2\) laser is shown in Fig. 3. Measurements of the damping time of the absorption pulse give the time of the \( V-T \) relaxation directly for the vibration \( v_2 \) in ammonia. It must be noted, however, that the addition of the thermal part of the UV absorption pulse can distort the real value of \( T_{V-T} \). In relaxation measurements, therefore one has to pay close attention to this fact.

Actually, measurement of the value of \( pT_{V-T} \) in the range of NH\(_3\) pressures in the cell from 10 to 15 Torr gives a value of \( 2.5 \pm 0.5 \text{ nsec-atm} \) (see also\(^8\)). (The duration of the pulse was measured at the height at which the amplitude had decreased by a factor \( e \).) For high ammonia pressures in the cell, the contribution of the thermal part of the pulse becomes important; it now greatly increases the measured value of \( T_{V-T} \) (Fig. 3). The limitations on the lower-limit pressure are not of significance and are due only to the sensitivity of the apparatus.

The increase in the sensitivity of the apparatus by about an order of magnitude (compared with\(^8\)) allowed us to carry out relaxation measurements in NH\(_3\) gas at a minimal pressure in the cell of 1–2 Torr, which gave a value of \( 1.9 \pm 0.2 \text{ nsec-atm} \) for \( pT_{V-T} \). This value was obtained by averaging over 30 oscillograms.

In order to eliminate the contribution of heating of the gas by the laser radiation in measuring the vibrational-translational relaxation time in ammonia, we also made measurements of the time \( V-T \) after strong dilution of the ammonia by an inert gas (ballast). In this case, the relaxation time \( T \) of the mixture will be determined by the expression

\[
\frac{1}{T} = \frac{p_{\text{NH}_3}}{T_{\text{NH}_3-\text{NH}_3}} + \frac{p_B}{T_{\text{NH}_3-B}},
\]

where \( p_{\text{NH}_3} \) and \( p_B \) are the partial pressures of the ammonia and the ballast in the cell (in Torr);

\( T_{\text{NH}_3-\text{NH}_3} \) and \( T_{\text{NH}_3-B} \) are the relaxation times in pure ammonia and in the ammonia-ballast mixture, respectively, at a pressure of 1 Torr. If we plot \( 1/T \) against \( p_B \), the slope of the straight line gives the value of \( 1/T_{\text{NH}_3-B} \), and the segment that it intercepts on the ordinate axis gives the value of \( p_{\text{NH}_3}/T_{\text{NH}_3-\text{NH}_3} \).

Such a plot is shown in Fig. 5. As ballasts we used argon, xenon, and oxygen, the pressures of which in the mixture were varied over the range 50–760 Torr. In working with argon and xenon, the ammonia pressures in the cell amounted to 2 and 3 Torr, respectively, and to 6 Torr when oxygen was used as a ballast. The results obtained for \( pT_{\text{NH}_3-\text{NH}_3} \) and for \( pT_{\text{NH}_3-B} \) are given in Table I.
Discussion of results. The vibrational-translational relaxation time in the ammonia molecule has been measured in many studies—see Table II. If we also consider the early studies here, the results will vary over two or three orders of magnitude. A critical review of the data on TV - T in ammonia as measured by the method of ultrasonic dispersion, and also of the values of TV - T at various temperatures of the ammonia, is given in the paper of Bass and Winter.\footnote{6} These authors give the value of 2.5 ± 0.8 nsec-atm for the vibrational-translational relaxation time in the NH₃ molecule at a temperature of 300°K, which agrees, within the limits of experimental error, with the result obtained in the present study. Data on the vibrational-translational relaxation in mixtures of ammonia with other gases are lacking in the literature. However, it was noted by Knottel\footnote{10} that the addition of water or ammonia to oxygen sharply reduces the relaxation time of the latter (see also\footnote{17}). The authors cite the following values for the relaxation times: \( p_{T_{V-T}} = 3.2 \times 10^4 \text{nsec atm} \), \( p_{T_{V-T}} = 130 \text{nosec-atm} \) at 288°K.

These authors give the value of 2.5 \( \pm \) 0.8 nsec-atm for the vibrational-translational relaxation time in the ammonia molecule. This gives rise to a strong dependence of the probability \( P \) of the V-T process on the orientation of the colliding molecules. If the probability of V - T relaxation is \( P_0 \) for a nonpolar molecule, then it is equal to \( P = \Phi P_0 \) for a polar molecule, where the factor \( \Phi \) takes into account the self-orientation of the molecules in the collision process. The large value of the factor \( \Phi \) for ammonia molecules is what leads to the small value of the vibrational-translational relaxation time. An increase in the temperature of a polar gas will decrease the self-orientation factor of the molecules in the collision process, which leads to an anomaly in the temperature dependence \( P(T) \).\footnote{5}

However, the experimental temperature dependence differed significantly from the dependence obtained by Shin. Therefore, in\footnote{21}, Shin considered the problem within the framework of the vibrational-rotational relaxation model, which leads to agreement with the experimental results within the limits of experimental error.

The essence of the dimer model is as follows: because of hydrogen bonding, the vibrationally excited ammonia molecule forms a dimer with a molecule of NH₃ in the ground state. There is then a transfer of vibrational energy to the newly formed oscillator of two ammonia molecules (the dimer). Such a model was, in particular, considered by Shin for the molecule HF.\footnote{18}

4. MEASUREMENT OF EXCITATION TRANSFER

Fraction of the energy transferred in an isotopic mixture of ammonia molecules. Experiments with measurement of the population of the level \( \nu' = 1 \); \( \bar{X} \) in the presence of a buffer gas at various ammonia pressures showed that at high buffer-gas pressures, the population of this level does not depend on the pressure of the ammonia in the cell in the range 3-12 Torr, and varies linearly with the pressure of the buffer gas. Figure 6 gives the dependence of the population of the level \( \nu' = 1 \); \( \bar{X} \) on the pressure of the buffer gas (argon) at ammonia pressures in the cell of 6 and 12 Torr. It is seen that the population of the level \( \nu' = 1 \); \( \bar{X} \) becomes constant beginning at an argon pressure in the cell of 200 Torr.

![FIG. 5. Dependence of reciprocal relaxation time on the ballast pressure: ---6 Torr NH₃ + O₂, ---3 Torr NH₃ + He, 0-2 Torr NH₃ + Ar.](image)

![FIG. 6. Dependence of population of the level \( \nu' = 1 \); \( \bar{X} \) on the pressure of the buffer gas (argon) at ammonia pressures in the cell of 6 and 12 Torr.](image)
The dependence of the population of the level $v'' = 1$; $X$ of the NH$_3$ molecule on the pressure of the buffer gas (argon) at various ammonia pressures in the cell can be understood by considering the process of filling of this level by laser radiation through a single vibrational-rotational transition (the "bottleneck" effect\cite{22,23}). The maximum rate of input of vibrational energy exists under the condition

$$\sigma I^{\text{rot}} \gg 1$$

(1)

and is determined by the expression\cite{22}

$$W = (2\sigma I^{\text{rot}}/q)^{1/2},$$

(2)

where $\sigma$ is the cross section of the vibrational-rotational transition, which depends on the pressure of the ammonia and the buffer gas in the cell as a consequence of the collision broadening of the vibrational-rotational absorption lines; $I$ is the intensity of the laser radiation [photons/cm$^2$·sec];

$$I^{\text{rot}} = \frac{\sigma \nu}{2} \frac{P_{\text{NH}_3}}{\tau_{\text{rot}}^{\text{NH}_3}} + \frac{P_{\text{B}}}{\tau_{\text{rot}}^{\text{B}}}$$

is the rotational relaxation time in the gas mixture; $P_{\text{NH}_3}$ and $P_{\text{B}}$ are the ammonia and buffer-gas pressures (Torr) and, by virtue of the fact that the times $\tau_{\text{rot}}^{\text{NH}_3}$ and $\tau_{\text{rot}}^{\text{B}}$ are comparable at high ballast pressures, $\tau_{\text{rot}}^{\text{rot}} = \tau_{\text{rot}}^{\text{NH}_3} B / P_{\text{B}}$; $q$ is the fraction of the particles at the operating rotational sublevel.

Consequently, at low populations of the vibrational level ($n_i \ll n_0$) we have for the maximal filling in the presence of the ballast

$$n_i = n_0 \frac{q}{2} \frac{\tau_{\text{rot}}^{\text{rot}}}{\tau_{\text{rot}}^{\text{B}}}$$

(3)

where $\tau_{\text{rot}}^{\text{rot}}$ is the duration of the laser pulse (in the case considered, $\tau_{\text{rot}}^{\text{rot}} \gg \tau_{\text{rot}}^{\text{B}}$) and $n_0$ is the population of the ground state. Thus, at pressures of the buffer gas such that the cross section $\sigma$ becomes large enough so that the condition (1) is satisfied, the population of the vibrational level does not depend on the ammonia pressure and changes linearly with the pressure of the buffer gas.

The independence of the population of the level $v'' = 1$; $X$ of the ammonia pressure in the cell was used by us to measure the fraction of the energy transferred from one ammonia isotope to the other in the pumping of one of them by the IR laser radiation. A mixture of $^{15}$NH$_3$ + $^{15}$NH$_3$ with the ratio 1:1 was studied. Only the $^{15}$NH$_3$ was excited by the laser radiation, and the total filling of the vibrational level $v'' = 1$ of the molecules $^{15}$NH$_3$ and $^{15}$NH$_3$ was determined from the UV absorption.

The appearance of an excess population of the level $v'' = 1$ in comparison with the case of excitation of the single-component mixture with $^{14}$NH$_3$ indicates the transfer of vibrational excitation from $^{14}$NH$_3$ to $^{15}$NH$_3$ during the course of the laser pulse. The excess filling quantitatively describes the fraction of the vibrational energy transferred from the $^{14}$NH$_3$ molecules to the $^{15}$NH$_3$ molecules. A typical experimental dependence is shown in Fig. 6.

Estimate of the rate of $V$-$V$ exchange on the basis of the fraction of transferred energy. We consider the process of exchange of vibrational excitation in an equimolar isotopic mixture of molecules under the condition that the concentration of the molecules vibrationally excited by the laser radiation remains constant, which was also the case in the experiment described above. We shall consider the following processes:

$$A_1' + A_2' \rightarrow A_3' + \lambda_1,$$

(4)

$$A_2' + A_3' \rightarrow A_1' + \lambda_2,$$

(5)

$$A_1' + A_0 \rightarrow A_2' + \Delta E,$$

(6)

$$A_2' + A_0 \rightarrow A_1' + \Delta E,$$

(7)

where $\lambda_1$, $\lambda_2$, $\lambda_0$ are the isotopic molecules, and the molecule $A_1'(A_2')$ is excited by the laser radiation; $M$ is the ballast molecule; $k_{01}$, $k_{02}$ are the rate constants of exchange of vibrational excitation; $k_{01}$, $k_{02}$, $k_{0M}$ are the rate constants of vibrational-translational relaxation due to collisions with molecules of the other isotope, between molecules of the same isotope, and with molecules of the buffer gas, respectively, $\Delta E = \hbar \omega$ is the vibrational-quantum energy transferred as a result of collision to other degrees of freedom. We put the concentrations $[A_1] = [A_0] = N$, $[M] = M$. Taking the processes (4)–(7) into account and considering the stationary case, we get for the fraction of transferred quanta

$$\alpha = \frac{[A_1']}{[A_1]} = \frac{1}{1 + \frac{2k_{01}N + k_{02}M}{k_{0M}}},$$

(8)

where $k_{01} = k_{02}$, $k_0 = k_0'$ and it is assumed that $[A_1'] \ll [A_1]$. Or, in terms of the relaxation times for unit concentrations of the particles, $T_{A-A} = 1/k_{01}$, $T_{A-M} = 1/k_{0M}$. $T_{V-V} = 1/\lambda_1$, $T_{V-T} = 1/\lambda_2$, and $T_{V-M} = 1/\lambda_0$.

$$\alpha = \frac{1}{1 + 2T_{V-V}/T_{V-M}},$$

(9)

where $1/T_{V-V} = 2N/T_{A-A} + M/T_{A-M}$ is the probability of vibrational-translational relaxation in the isotopic mixture of ammonia and ballast.

Figure 7 shows the experimental and computed dependences of the fraction of transferred energy $\alpha$ on the ballast pressure. The calculations were carried out for different values of $T_{V-V}/T_{V-M}$. It is seen from Fig. 7 that the time of vibrational-exchange in ammonia amounts to $T_{V-V} = 1.2 \pm 0.4$ nsec atm ($T_{V-T} = 1.9 \pm 0.2$ nsec atm).

Discussion of the results on V-V exchange. The coupling of the times of V-V and V-T relaxations with the fraction of transferred energy was obtained under the assumption of stationarity of the process. A more exact machine calculation, taking also into account the process of pumping of one of the isotopes by the laser radiation and the form and duration of the laser pulse in the experiment, leads to a similar result. Thus, taking into consideration the processes (4)–(7), one can obtain an estimate of the time of V-V exchange by the IR-UV resonance method.

However, the value obtained for $T_{V-V}$ can turn out to be much smaller for the case of formation of dimers in ammonia. It is known that the molecules of ammonia are capable of forming dimers by hydrogen bonding. Thus, for example, at room temperature the relative

FIG. 7. Experimental (points) and calculated (curves) fractions of transferred energy in the isotopic mixture ($^{14}$NH$_3$ + $^{15}$NH$_3$) with pumping of $^{14}$NH$_3$ by the radiation of a CO$_2$ laser as functions of the ballast (Ar) pressure. The calculated curves 1, 2 and 3 correspond to $T_{V-V}/T_{V-T} = 0.5, 0.67$, and 1.0, respectively.

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number of dimerized molecules amounts to $\sim 2.3 \times 10^{25}$. If dimerization takes place on collision when one of the colliding molecules is vibrationally excited, then, as a result of a decrease in the energy of activation for the dimerization process by $\sim 1000 \text{ cm}^{-1}$, dimers in the excited state can be formed in each collision. The time of V-V exchange in such a dimer can be very small. If such a dimer has a lifetime $\tau_{V-v}$, then even under satisfaction of the condition $\tau_V \ll \tau_{V-v}$ the fraction of the energy $\alpha$ that is transferred from one ammonia isotope to the other (in a 1:1 isotope mixture) will be $\frac{\alpha}{\alpha'}$, as is clear from the statistics of the collisions. In this case, it is not possible to infer the time of V-V exchange between isotopes on the basis of the fraction of transferred energy.

To establish the selectivity of isotope separation by two-step dissociation, it suffices to know only the fraction of transferred energy.

Thus, the method of double IR-UV resonance allows us to investigate the kinetics of the vibrational excitation of molecules, i.e., to obtain the data necessary for carrying out selective chemical reactions with laser radiation.

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