IR fragmentation of clusters of C_2H_5Cl molecules

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The evolution of the IR absorption spectrum during the gas-(condensed state) transition in the course of the clustering of C_2H_5Cl molecules has been studied experimentally. Spectra of the IR absorption cross section and the cross sections for the decay of dimers and trimers of this molecule in a gas-dynamically cooled supersonic molecular beam have been measured. The intracluster relaxation times of the molecular vibrations v_9 and v_8 in dimers and trimers of this molecule have been measured.

In this letter we are reporting observation of the spectrum of the IR-laser dissociation of dimers and trimers of the C_2H_5Cl molecule in the linear absorption region of the gas and liquid phases of this substance. Many-photon absorption of the C_2H_5Cl molecule has been studied previously.[1]

The major parts of the experimental apparatus[2] are a time-of-flight mass spectrometer,[3] a TEA CO_2 laser, and apparatus for monitoring the frequency and energy of the laser light and the temporal parameters of the measurement cycle of the system. In addition, we use a pulsed source of a supersonic molecular jet ($\tau_{pulse} \sim 300$ μs), a unit of skimmers which forms a molecular beam with a cross section of 4×15 mm in the zone of the ion source, a three-channel CAMAC system for detecting the charge in a given mass peak, and an ion-beam energy filter, which makes possible measurements by the retarding-potential method[4] and also a strobing of the detector timed in accordance with a selected mass packet.

The measurement cycle of the system includes a stage in which the pulsed molecular beam is formed, a transverse illumination of this beam, and a mass-spectral analysis of the illuminated zone. A statistical database was constructed from 20 measurement cycles.

The pressures in the receiver and in the ion source were respectively 500 torr and 10^{-7} torr. The Mach number, the temperature, and the velocity of the beam were $M \simeq 11$, $T \simeq 30$ K, and $V \simeq 560$ m/s. Under these conditions, we observe a condensation in a molecular beam 4 mm wide; this condensation corresponds to the appearance of dimers and trimers which are concentrated in the axial plane of the beam, with a profile 1 mm wide. This part of the beam is the entity from which we obtained the spectral data on the cluster decay cross sections.

The procedure for obtaining the cross sections for the decay of the dimers and trimers of C_2H_5Cl can be outlined as follows: The relative number of clusters which

have not dissociated (Q_L/Q_0) is found experimentally as a function of the radiant energy density Φ_L for each line of the CO_2 laser. Figure 1 shows some of these curves, corresponding to the center and wing of the absorption of the clusters in the "red" part (gas, ν_9) and the "violet" part (liquid, ν_8) of the linear absorption spectrum of C_2H_5Cl. In the case of a linear absorption of the laser light, the logarithm of this quantity should be proportional to the energy of the laser pulse. The cluster decay cross sections were accordingly determined from the slopes of straight lines fitted by the method of least squares to the points in the plot of $\ln (Q_0/Q_L)$ versus Φ_L. We see that in some cases there are points which do not conform to these straight lines, even when we allow for the statistics of the measurements. If we rule out the possibility of long-term instrumental fluctuations, which are ignored in the statistical analysis of the experimental results, we conclude that the explanation for this effect is as follows. In the linear absorption spectrum of a cluster there may be narrow peaks due to long-lived states of a cluster within the wide Lorentzian line. The spectral positions of these peaks may vary in a strong field by virtue of the quadratic Stark effect. As they move with respect to the laser line as the field intensity is varied, these peaks may cause the observed changes in the cross section. A linear approximation of the dependence $\ln(Q_0/Q_L) \sim \Phi_L$ eliminates the influence of this effect. Note also that the straight lines do not go through the origin, apparently because of an increase in the charge in the mass peaks of the dimer and the trimer at small values of Φ_L, at which the decay of the very small number of n-dimers outweighs the dissociation of M_2 and M_3.

Figure 2 shows the decay cross sections of $(C_2H_5CL)_2$ and $(C_2H_5Cl)_3$ clusters versus the frequency of the laser field. The width of the spectrum is determined by the shortest relaxation time: the intracluster relaxation time of the energy of the excited mode. In contrast with Casassa et al.,[5] we believe that the width of the spectrum found here contains information about the time scale of specifically this relaxation process, not the predissociation time of a cluster, which may be substantially longer. For dimers, these times (τ_d) are 1.4×10^{-12} and 1.8×10^{-12} s in the ν_9 and ν_8 regions,
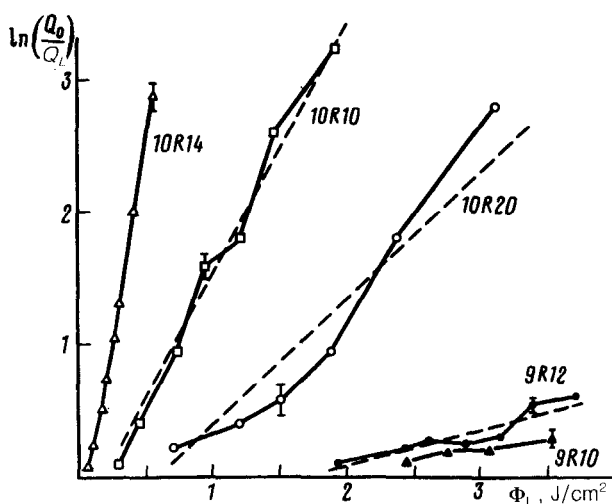

FIG. 1. Relative number of dimers which have not decayed, Q_0/Q_L, versus the radiant energy density of the laser light, Φ_L, for certain lines of a CO_2 laser, in the coordinates $\ln(Q_L/Q_0)$, □—10R10; △—10R14; ○—10R20; ●—9R12; ▲—9R10.
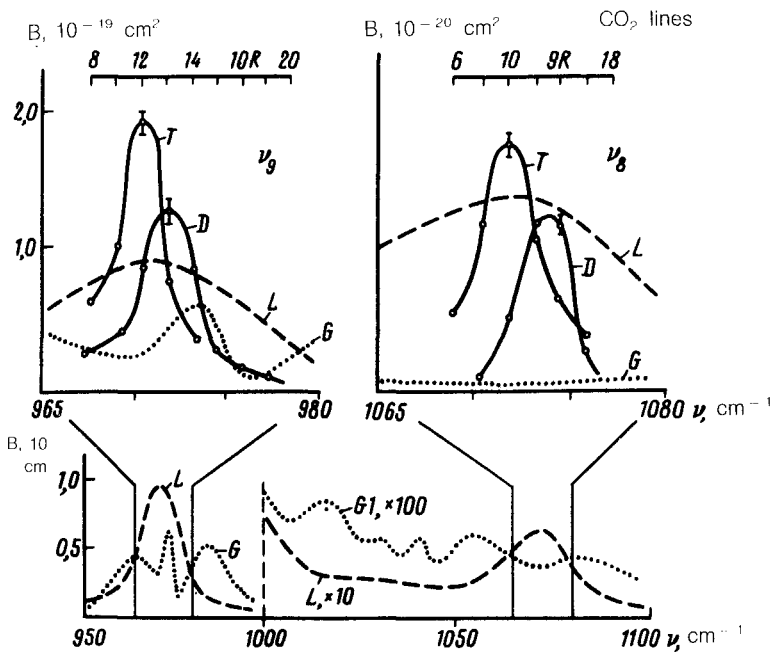
FIG. 2. Spectra of the decay cross sections of the dimer, D, and of the trimer, T, in the ν_9 and ν_8 bands. L— Data from Ref. 6 on the linear absorption in the liquid phase at layer thicknesses $\triangle = 60\ \mu$ and $\triangle = 200\ \mu$; $G\,1$—the same, but for the gas phase, with $P = 525$ torr and $\triangle = 69$ cm; G—absorption spectrum of the gas phase for $P = 30$ torr and $\triangle = 10$ cm.

respectively. Correspondingly, the times for the trimers (τ_t) are 2×10^{-12} and 1.7×10^{-12} s. As can be seen from the figure, an increase in the number of molecules in a cluster (n) is accompanied by a shift of the resonance absorption in the long-wave direction and by an increase in $\sigma \sim n$. The evolution of the frequency dependence in the region corresponding to the dipole-weak active mode ν_8 of the molecule illustrates the formation of a dipole absorption spectrum during the clustering of gas molecules due to a change in the symmetry of the entity.

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