

Structure of C_3 as Measured by the Coulomb-Explosion Technique

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(Received 28 January 1986)

By application of the Coulomb-explosion technique with a new type of detection system, the structure of the neutral C_3 molecule has been studied. The detector allows for the first time simultaneous determination of the velocity vectors of all nuclei involved, from which correlation between internal degrees of freedom in the molecules can be derived.

PACS numbers: 35.20.-i

Studies on the dissociation of fast (megaelectron-volt) molecular-ion beams in thin foils suggest¹⁻³ a novel alternative approach to the determination of molecular structure. In such experiments, individual molecular projectiles rapidly lose many electrons and the monatomic highly charged fragments repel each other via the Coulomb force ("Coulomb explosion"). The final-state momentum distribution of each molecule is measured and related to the initial molecular structure. In this particular investigation a new type of detection system has been utilized which allows, for the first time, simultaneous determination of the velocity vectors of all nuclei involved without introduction of any bias depending on geometry or orientation.⁴

The main tool for the obtaining of structural information on isolated molecules is spectroscopy. The observed spectral lines are analyzed by use of a vibrational-rotational model, which assumes small displacements from the equilibrium position, and different time scales between rotational and vibrational motions. Although this model was found to be very useful when combined with perturbation methods, there are many interesting systems for which it is not valid. Among those are "floppy" systems (some of the van der Waals complexes, for example), or molecules that are highly vibrationally excited. In these cases, because of the large amplitude vibrations, the interaction between rotation and vibration becomes important, and the conventional spectroscopical analysis is not possible. For these systems an alternative method for structural verification is very desirable.

In this work the structure of the neutral C_3 molecule was studied as a first demonstration of the technique and its capability.⁵ The molecule C_3 was chosen because of both experimental convenience and its theoretical interest. Gausset and co-workers⁶ analyzed the 4050-Å band, observed also in spectroscopic studies of comets, as an electronic transition in the linear

C_3 molecule. The ground electronic state was assigned as a ($^1\Sigma$) state, which has a very low-frequency bending mode (63 cm^{-1}) and asymmetric and symmetric stretching vibrations with wave numbers of 1230 and 2040 cm^{-1} , respectively. Recent theoretical work⁷ confirmed the linear structure, and concludes that the C—C—C bond angle can be changed by a large amount from its equilibrium value, with a very small change in either energy or bond length. The large-amplitude bending combined with the availability of existing experimental and theoretical works makes the C_3 system an interesting test case for the new technique.

The Pelletron accelerator at the Weizmann Institute is equipped with a sputter ion source in which C_3^- is produced when a graphite target is bombarded with Cs atoms. The negative carbon clusters are then injected, after mass selection, into the accelerating region, in which they reach energies of 4 MeV per atom. At the center of the accelerator, in a field-free region, an electron is stripped by a N_2 gas stripper, operated at a pressure corresponding to the single-collision regime. The neutral C_3 molecules thus formed continue further with the same velocity for about 20 m, while the charged particles are swept away by a magnet. The neutral molecules impinge upon a thin ($200\text{-}\text{Å}$) carbon foil, which strips many of the electrons, a process followed by dissociation of the system and the production of carbon ions in different charge states. A small magnet deflects the carbon beams, according to their charges, into three detectors situated 2.1 m below the carbon foil.

The detector array was built from three parts, each of which is a $5\times 5\text{-cm}^2$ multiwire gas detector.⁸ A full description of the detector will be given elsewhere.⁹ The spatial resolution of the detector was measured by insertion of a mask with 0.5-mm-diam holes in front of the detector, and was found to be better than 1 mm. The time resolution was found to be better than 1

nsec. Time and two-dimensional position information were recorded for each of the three particles arriving simultaneously at the detector with charge states 2+, 3+, and 4+, respectively.

The overall performance of the detector system was checked by our measuring the Coulomb explosion of C₂ molecules. The bond length extracted for this system agreed within 2% with the one reported in the literature.¹⁰ The C₂ data were also used to determine the target thickness and the effective average charge of the carbon ions inside the target. Under the assumption that the C₂ molecule is not excited vibrationally to very high states, the observed angular distribution width is mainly due to multiple scattering in the carbon foil. This effect depends in a well-known fashion on the target thickness, and thus can serve as a good indicator of the thickness. The part of the Coulomb explosion that occurs inside the foil, and the average charges of the two carbons, can be obtained by plotting of the square of the angle between two emerging carbon ions as a function of the product of the charges, and extrapolation of the straight line thus obtained to a charge product of zero. The angle at this point determines the fraction of the Coulomb explosion occurring in the foil. When we switched to C₃, time and position information was recorded for each event where three carbon ions with the charges 2+, 3+, and 4+ arrive at the detector simultaneously.

The information thus obtained can be reduced to three independent structural parameters, either in the velocity space of the carbon ions (*v* space), or in the spatial coordinate frame of the initial neutral molecules (*r* space). However, it is important to note that the Coulomb energy is an invariant in both representations; therefore it was chosen as one of the parameters. It is also important to note that while the transformation from *r* to *v* space is unique, the reverse

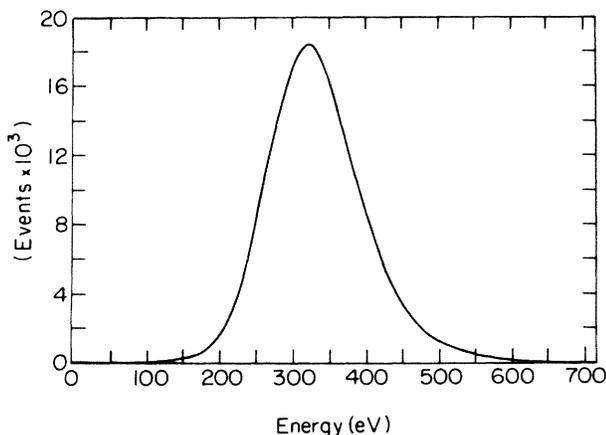


FIG. 1. The total Coulomb energy spectrum.

transformation is not, except for a few regions in the *r* space. Hence an analysis of the data has to involve parametrization of the *r*-space probability distribution.

The observed distribution of the final kinetic energy is shown in Fig. 1. The total energy is given by $(1/6m) \sum_i v_i^2$, where v_1 , v_2 , and v_3 are the measured relative velocities between C²⁺ and C³⁺, C³⁺ and

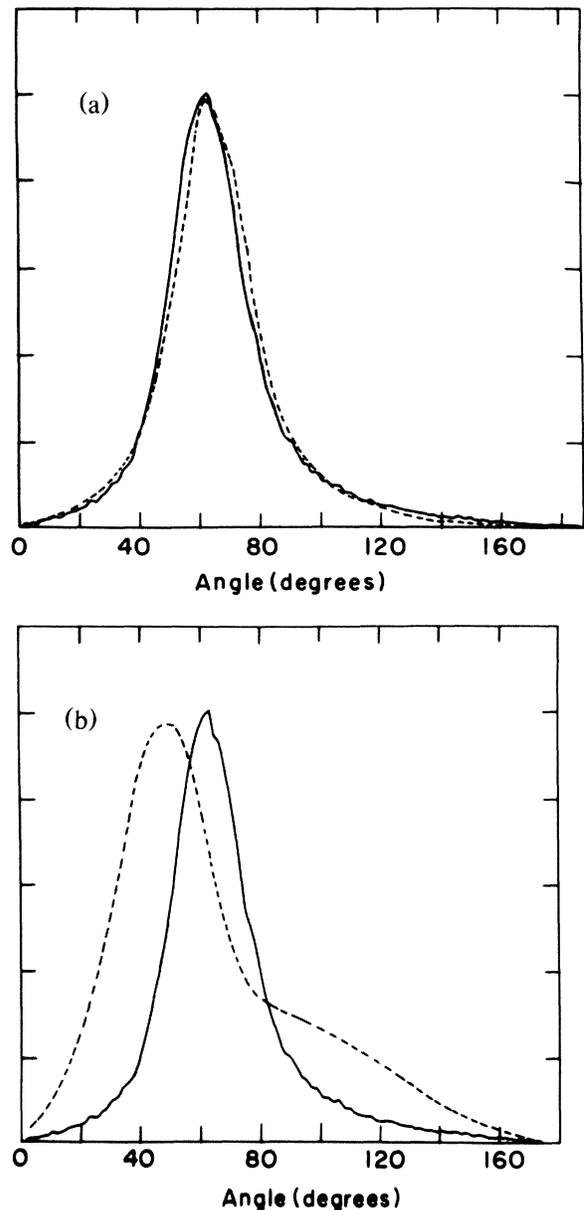


FIG. 2. The data presented as a function of the angle between the direction of the initial velocity and the velocity following the Coulomb explosion (solid line). (a) A distribution resulting from the computer simulation, assuming a vibrational temperature of 500 K (broken line). (b) The distribution corresponding to a vibrational temperature of 100 K for comparison (broken line).

C^{4+} , and C^{2+} and C^{4+} , respectively. The total energy of the Coulomb explosion of a molecule is inversely proportional to the dimension of the original molecule. Once the shape of the molecule is determined (or assumed), the length of the chemical bonds can be deduced by the total explosion energy. If the C_3 molecule is assumed to be linear, with two equal bonds (see below), then the peak in Fig. 1 (330 eV) yields a bond length of $1.25 \pm 0.05 \text{ \AA}$, which is consistent with the value reported previously.^{6,11,12}

The width of the distribution ($\sim 40\%$) is governed by the multiple scattering of the carbon ions due to the $4\text{-}\mu\text{g}/\text{cm}^2$ target foil. Therefore, no fine determination of the bond-length distribution is possible. It can be shown that by use of $0.1\text{-}\mu\text{g}/\text{cm}^2$ target foil (recently becoming commercially available) the zero-point fluctuation width of the stretching mode can be accurately measured and correlated to the other degrees of freedom of the molecule.

Even with the severe limitation due to the multiple scattering, the experiment was highly sensitive to the C—C—C bond angle. In order to demonstrate it the data are presented as a probability distribution in v space with the following two different sets of coordinates: (I) the angle between the directions of v_1 and v_2 [Fig. 2(a)], and (II) two dimensionless parameters $a = v_1^2 / \sum_i v_i^2$, $b = v_3^2 / \sum_i v_i^2$ [contour plot Fig. 3(a)]. Simulation of the data was carried out by parametrization of the molecular structure in r space, followed by Coulomb trajectory transformation to v space. Finally, the proper multiple scattering was folded in. For simplicity, we have assumed an ensemble of linear molecules with vibrational frequencies at thermal equilibrium as given in Ref. 5. By variation of the temperature it was found that the data could be best fitted by a vibrational energy distribution corresponding to 500 K as shown in Figs. 2(a) and 3(b). It is illuminating to compare these results with the simulated distributions for a temperature of 100 K [Figs. 2(b) and 3(c)]. The limit of an unbent linear structure is characterized in the contour plot by three distinct points in which the relative velocity between the two outer atoms is about twice as much as the other two relative velocities. The three peaks in Fig. 3(c) are reminiscent of such a linear structure, smoothed by multiple scattering and finite temperature.

The capability of the Coulomb-explosion method to determine the structure of three-atom molecules was investigated in this work. For the study reported here, it was the multiple scattering of the carbon ions in the target material that imposed severe limitations on the overall experimental resolution. With the thinner foils now becoming available a much better resolution is expected. The prospect of such an experiment to reveal correlation between molecular degrees of freedom is unique and intriguing. The initial step in this direc-

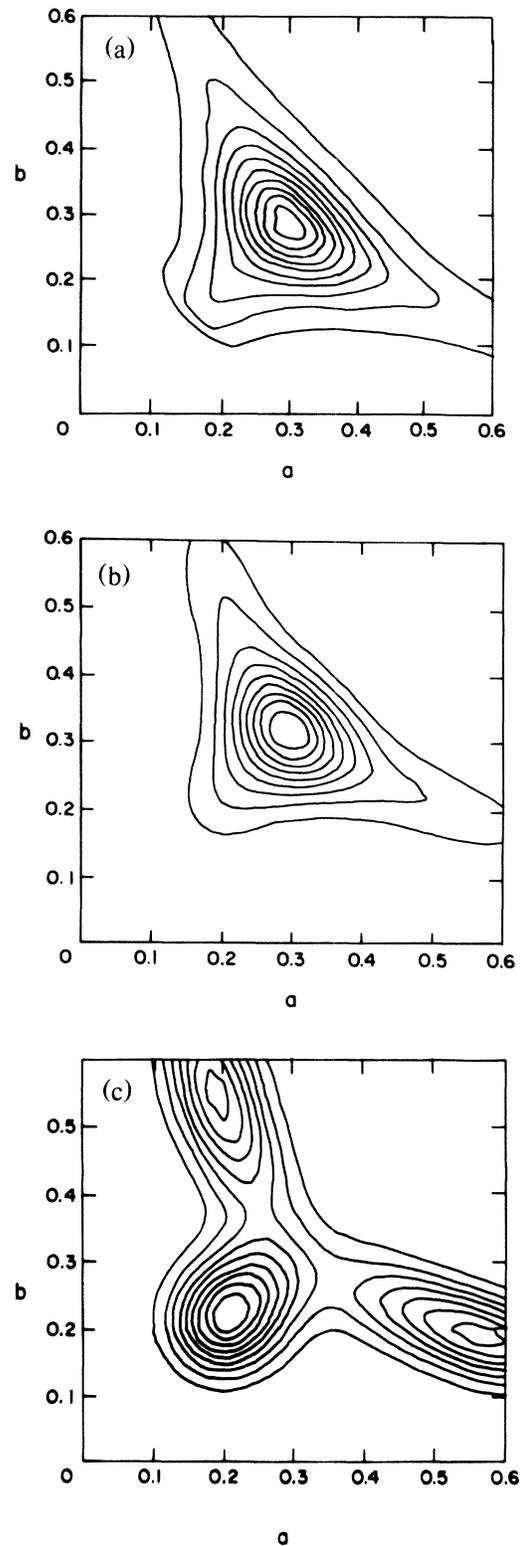


FIG. 3. (a) The data presented as a function of two dimensionless parameters $a = v_1^2 / \sum_i v_i^2$ and $b = v_3^2 / \sum_i v_i^2$. (b), (c) Computer simulations assuming vibrational temperatures of 500 and 100 K, respectively.

tion was taken in the present study where both the abilities of the method and its limitations were demonstrated.

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