Dissociative recombination and excitation of D_3^+

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Measurements of the dissociative recombination of deexcited D_3^+ ions yield cross sections similar at low energies to those found for H_3^+ [H. Hus *et al.*, Phys. Rev. A **38**, 658 (1988)]. Previous measurements [J. B. A. Mitchell *et al.*, J. Phys. B **17**, L909 (1984)] performed with excited ions indicated that there was an isotope effect giving rise to a larger cross section for H_3^+ than for D_3^+. This effect can in fact be explained in terms of differing vibrational-state populations in those studies rather than by molecular-dynamics arguments. Dissociative excitation measurements for D_3^+ are found to contain a wealth of resonance structure.

INTRODUCTION

The dissociative recombination of H_3^+ is of considerable importance in a number of applications, including interstellar and planetary atmospheric chemistry, thermonuclear fusion, and high-current-ion-source research. The recombination of D_3^+ is particularly important in the latter two applications. It is also of interest to examine the recombination of isotopic partners in order to obtain a clearer understanding of this complex phenomenon.

A review of the status of H_3^+ recombination may be found in several papers in Ref. 1, and the subject has been addressed more recently by Mitchell,[2] Van der Donk *et al.*,[3] Amano,[4] and Canosa and co-workers.[5,6] Previous measurements by Mitchell *et al.*[7] addressed the subject of the effects of isotopic change on the dissociative recombination of triatomic hydrogen ions and found that the cross section diminished as the deuterium content of the ions increased. This effect was explained qualitatively in terms of a mass dependence for the survival factor. This quantity denotes the probability that the intermediate neutral compound state, formed in the electron-capture process, does not autoionize before the state can be stabilized dynamically, i.e., by converting potential into kinetic energy and thus dropping the potential energy of the state below the ionization potential. The results presented in this paper indicate that this explanation is not the major reason for the observed difference in the cross sections with isotopic change.

EXPERIMENTAL METHOD

The merged electron-ion-beam apparatus at the University of Western Ontario was used for the measurements. This technique has been described in detail elsewhere[8] and will only be outlined here. Ions are produced using a radio-frequency ion-trap source[9] mounted in the terminal of a 400-keV Van de Graaff accelerator. In this source, ions are produced by electron-impact ionization of the source gas and these ions are confined to a U-shaped canal along which they drift randomly until they reach the exit, which is arranged in the form of an octupole lens. In front of this lens is an extraction electrode to which a potential of up to 100 V can be applied. The application of this potential results in a larger beam current, but it is our experience[7,9–11] that when the source is operated with a very low (<10 V) extraction potential, the resulting beam contains ions with very low internal energy. The reason for this is twofold. First, the low extraction potential allows ions to remain longer in the source, giving them more time to make deexciting collisions. Second, a high extraction potential can lead to the excitation of the emerging ions due to collisions with the source gas. The source is typically operated at a pressure of 0.1 Torr and the gas is usually a hydrogen-helium-argon mixture. In this case, deuterium was substituted for the hydrogen.

Once formed, the beam is accelerated and mass analyzed before being injected into the merged-beam apparatus. This consists of an ultrahigh vacuum (10^{-10} Torr) chamber within which the electron beam is produced using an indirectly heated barium oxide cathode. The beam is confined using a 25-G magnetic field and initially travels parallel to the ion beam. The electrons are made to merge with the ion beam using a combination of a transverse electric field and the axial-guiding magnetic field in a device known as a trochoidal analyzer. The beams overlap for a distance of 8.6 cm before the electrons are separated using a second trochoidal analyzer. The beam overlap is monitored in two places in the interaction region by scanning horizontally and vertically with movable vanes. The resulting changes in the ion- and electron-beam intensities are monitored and the currents are differentiated electronically in order to obtain profiles of the two beams in two dimensions, the effective collision area subsequently being determined.[12] The ion beam is deflected electrostatically into a Faraday cup and the neutral species resulting from collisions in the interaction region pass undeflected to be collected on a surface-barrier detector. Neutral species formed via interactions between the ion beam and the background gas are distinguished from those arising from electron-ion collisions by modulating the electron beam and counting the signals in and out of phase with the modulation. The

true signal is then determined by subtraction.

The collision cross section σ is determined using the formula

$$\sigma = \frac{C_n e^2}{I_i I_e L} \frac{|\mathbf{v}_i \cdot \mathbf{v}_e|}{|\mathbf{v}_i - \mathbf{v}_e|} F ,$$

where C_n is the neutral count rate; e is the electronic charge; I_i, $\mathbf{v}_i$, I_e and $\mathbf{v}_e$ are the ion and electron currents and velocities, respectively; L is the length of the interaction region; and F is the effective collision area, sometimes known as the form factor. The collision energy in the center-of-mass frame is obtained from

$$E_{\text{c.m.}} = (E_e^{1/2} - E_+^{1/2})^2 ,$$

where $E_+ = E_i m_e / m_i$ is known as the reduced ion energy. In practice, the ion energy is held fixed and the electron energy is varied in order to measure the cross sections as a function of center-of-mass energy. Recent studies[13,14] of H_2^+ recombination made using this apparatus have shown that the energy resolution is better than 5 meV. The ion- and electron-beam currents used in this measurement were typically 1×10^{-11} A and 30 μA, respectively.

The surface-barrier detector is energy sensitive and so is capable of distinguishing a single deuterium atom arising from dissociative excitation and carrying a third of the total beam energy from a triplet of deuterium atoms or a deuterium atom-molecule pair arising from dissociative recombination.

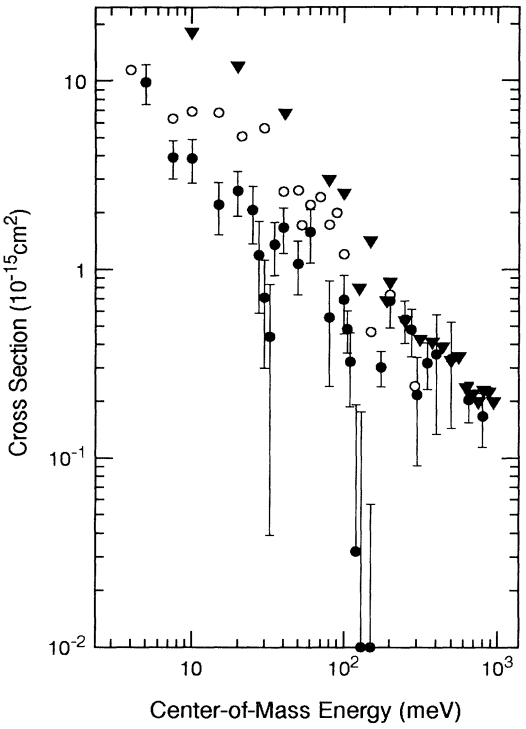

FIG. 1. Cross sections for the dissociative recombination of D_3^+. Solid circles, low-extraction results, see text; open circles, high-extraction results; solid triangles, rf-source results.

RESULTS AND DISCUSSION

Measured cross sections for the dissociative recombination of D_3^+ are shown in Fig. 1. The results taken for ions produced using a low source-extraction potential display two distinct resonance structures which are probably due to the influence of vibrationally excited levels of neutral Rydberg states lying just below the ion ground state. Such resonances have been seen by us in the case of H_2^+,[13,14] HeH^+,[10] and N_2^+,[11] although they were not apparent in our work on H_3^+. They have also been predicted theoretically in calculations for H_2^+,[15–17] CH^+,[18] and NO^+.[19] It has been our experience that such resonances are only seen when the ions used are in very low vibrational states.

Previous work in this laboratory[3,9] has shown that, when operated in the low-extraction-potential mode, the ion-trap source is capable of producing H_3^+ ions that are all in the $v=0$ level. It is expected therefore that this also applies to this measurement and that the results shown as solid circles in Fig. 1 refer to $v=0$ ions. The technique used to measure the internal energy of the H_3^+ ions was to examine the position of the threshold for the dissociative-excitation reaction

$$e + H_3^+ \rightarrow H + H_2^+ + e .$$

The reaction is studied by measuring the yield of hydrogen atoms as a function of energy. The threshold for this reaction is predicted to occur at 14.9 eV, and this is exactly where the onset was observed to occur for ground-state ions, although it was found that there were several resonant structures in the vicinity of this threshold. These resonances are presumably due to the temporary formation of a neutral resonance state lying in the vicinity of the excited-ion state. They have been discussed in more detail in Ref. 1.

In the present work, the same reaction was studied for D_3^+, the yield of deuterium atoms being monitored. The results are shown in Fig. 2. Here the situation is much

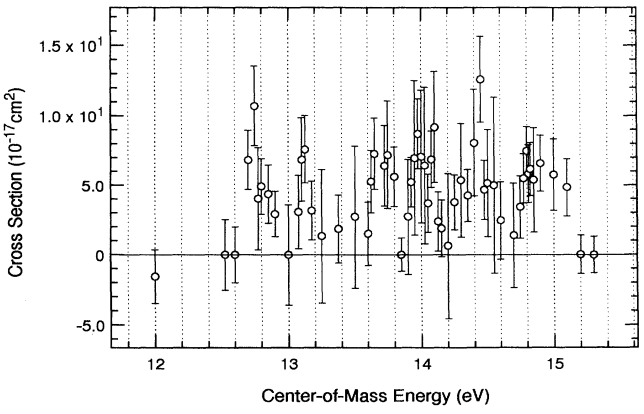

FIG. 2. Dissociative excitation cross sections for D_3^+.

more complicated. There is a wealth of resonances extending down to about 11 eV and it is not clear exactly where one could define a threshold for the direct-excitation process. Thus the exact internal energy of the D_3^+ ions cannot be determined. Given our experience with H_3^+, however, it can be surmised that they are in the $v=0$ level.

Also shown in Fig. 1 are cross sections for D_3^+ recombination, obtained using the ion-trap source in a high-extraction condition and using ions produced from a conventional rf ion source. It can be seen that the ion-trap high-extraction results lie just below the cross sections measured using an rf source. This was also found for H_3^+ in Ref. 9, where it was reported that there were no operating conditions where the ion-trap source produced results as high as those obtained using a conventional rf source. It is intriguing to note that there is evidence for the resonance at 100 meV appearing in these results as well as in the low extraction measurements.

In Fig. 3, cross sections obtained under low-extraction conditions using the ion-trap source and using a conventional rf source are shown for H_3^+ and D_3^+. It is very interesting to note that at low energy, the low-extraction ($v=0$) cross sections agree very closely, while the results measured using rf-source-produced ions differ by about a factor of 2. Previously,[7] this difference had been ascribed to an isotope effect that altered the recombination efficiency for the two ions. The data presented in Fig. 3 indicate that in fact this is not the case and that the difference in the rf cross sections is due to differing excited-state populations in the two ion beams. Table I, taken from the work of Anicich and Futrell,[20] lists the calculated population distributions of the vibrational energy for H_3^+ and D_3^+. Also listed are the energies of the various levels.

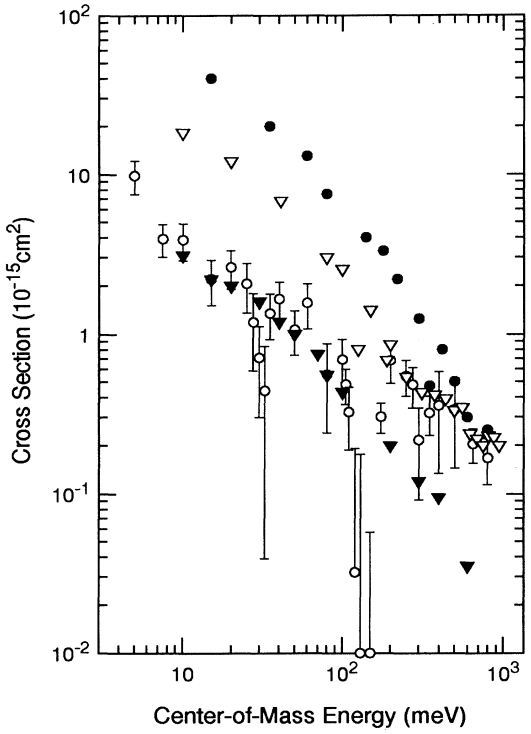

FIG. 3. Cross sections for the dissociative recombination of D_3^+ (open circles, low-extraction results; open triangles, rf-source results) and H_3^+ (solid triangles, low-extraction results; solid circles, high-extraction results).

It can be seen that the level spacing for D_3^+ is much less than that for H_3^+. This leads to a wider distribution of populated vibrational states with less concentration in the lower states and more in the higher. Blakley, Vestal, and Futrell[21] showed that the deactivation rate for H_3^+ ions in low vibrational states was much smaller than previously believed.[22–24] Thus for low v but $v \geq 2$, the deactivation rate is about 1×10^{-11} cm^{3}s^{-1}, while for $v=1$, the rate is closer to 1×10^{-12} cm^{3}s^{-1}. The calculated residence time for ions in the conventional rf ion source used in our measurements is about 35 μs. At an operating pressure of 0.1 Torr of hydrogen, this time is insufficient to ensure deactivation of such levels and so it is expected that this source will indeed produce ions in a range of vibrational states. This prediction was confirmed by dissociative-excitation studies.[9] In the ion-trap source, the residence time is of the order of milliseconds and it is possible to deactivate the H_3^+ ions and again this has been demonstrated.[3,9] Given the greater population of higher-lying vibrational states in D_3^+, it makes sense that these would be more rapidly deexcited, leading overall to a D_3^+ beam containing a lower population of excited states. This would explain the lower measured cross section for the rf-produced D_3^+ ions given that the cross section is seen to decline with decreasing vibrational quantum number.

TABLE I. Populations and energies of the vibrational states of H_3^+ and D_3^+ formed from H_2^+-H_2 and D_2^+-H_2 reactions (from Ref. 20).

v	H_3^+		D_3^+	
	Population	Energy	Population	Energy
0	0.0341	0.0	0.0106	0.0
1	0.0919	0.372	0.0290	0.261
2	0.1601	0.744	0.0556	0.522
3	0.2197	1.116	0.0853	0.783
4	0.2303	1.488	0.1156	1.044
5	0.1387	1.86	0.1424	1.305
6	0.0796	2.232	0.1587	1.566
7	0.0299	2.604	0.1483	1.827
8	0.0109	2.976	0.1146	2.088
9	0.0037	3.348	0.0672	2.349
10	0.0010	3.720	0.0396	2.610
11	0.0001	4.092	0.0187	2.871
12			0.0083	3.132
13			0.0035	3.393
14			0.0014	3.654
15			0.0001	4.176

A second interesting observation in Fig. 3 is the fact that above a few tenths of an electron volt, the H_3^+ and D_3^+ low extraction results diverge, the latter merging with the high extraction results. In other words, at these energies, the cross section is independent of vibrational state.

ACKNOWLEDGMENTS

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