J. Goldstone, and Dr. A. Guth for very beneficial discussions concerning Eq. (17).

[14] The charge $\alpha_s(\rho)$ is defined by the Pauli-Villars regularization. Its relation to the dimensionally regularized charge $\alpha_D(\rho)$ is $(\alpha_s/2\pi) \approx (\alpha_D/2\pi) + 9.5(\alpha_D/2\pi)^2$. Evidently α_D is not a suitable expansion parameter. This was recognized earlier; see V. Baluni, Phys. Rev. D 17, 2092 (1978).

[15] See, e.g., S. Weinberg, in *A Festschrift for I. I. Rabi*, edited by Lloyd Motz (New York Academy of Sciences, New York, 1977).

[16] This easily follows from the fact that instantons reduce the vacuum "energy density" by $\mathfrak{D}_{a(b)}(\rho_c)$ [cf. Eq. (15)]. Observe that in distinction to Ref. 12 the condition (18) is applied to the gas of instantons which are liberated by nonzero quark masses appearing in the Lagrangian (2) rather than constituent quark masses generated dynamically. The dynamically generated component of instantons was assumed to have a negligible effect for $\overline{\Delta}(0)$.

Discrete Energy Transfer in Collisions of Xe(nf) Rydberg Atoms with NH_3 Molecules

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In collisions with NH_3 molecules it is observed that Xe(nf) Rydberg atoms are selectively excited to discrete, more highly excited states. These states are identified by the technique of field ionization and are found to be displaced in energy from the initial Rydberg states by amounts equal to the rotational spacings of the NH_3 molecule. These measurements demonstrate, for the first time, the conversion of rotational energy to electronic energy in collisions.

Flannery[1] and Matsuzawa[2] have predicted that in collisions between Rydberg atoms and polar molecules rotational de-excitation of the molecules could provide the energy necessary to further excite or ionize the Rydberg atoms. To investigate this prediction we have made an experimental study of collisions between xenon Rydberg atoms Xe(nf) with $26 \leq n \leq 40$ and ammonia molecules.

The rotational term energies for NH_3 are given by

$$E_J = BJ(J+1) + (A-B)K^2, \qquad (1)$$

where J and K are rotational quantum numbers and A and B are constants. In dipole-allowed de-excitations ($J \to J-1$, $K \to K$) the energies released, ΔE_J, are approximately

$$\Delta E_J = E_J - E_{J-1} = 2BJ. \qquad (2)$$

If these energies are transferred to Xe(nf) Rydberg atoms, with term values T_n, the resulting states will have term values given approximately by

$$T_n' = T_n + 2BJ, \quad J = 1,\ 2,\ 3, \ldots. \qquad (3)$$

Clearly if $2BJ$ exceeds $|T_n|$, T_n' will be positive and ionization will occur, while for $2BJ$ less than $|T_n|$ further excitation will result.

For the particular case of Xe(27f) atoms the possible reactions are

$$\mathrm{Xe}(27f) + \mathrm{NH}_3(J)$$
$$\to \mathrm{Xe}^+ + \mathrm{NH}_3(J-1) + e^-, \quad J > 7; \qquad (4a)$$
$$\to \mathrm{Xe}(n'l') + \mathrm{NH}_3(J-1), \quad J \leq 7. \qquad (4b)$$

These processes are illustrated in Fig. 1. The arrows have lengths $2BJ$ with $J = 1, 2, 3, \ldots$) and widths which are proportional to the room-temperature populations of the upper rotational levels involved.

Collisions of the type (4b) lead to the production of seven discrete Rydberg states (or groups of states) which can be separately detected and identified by the technique of field ionization[3] since each of them will have its own characteristic critical field. This paper describes the first investigation of collisions of this type.

The apparatus has been described elsewhere[4] and only a few details will be discussed here. Xe $^3P_0$ atoms produced by electron impact excitation are excited, using a pulsed laser, to a selected Rydberg nf state in a region into which NH_3 target gas can be admitted. Approximately 7 μsec after each laser pulse, the electric field in the excitation region is increased from 0 to 1100 V/cm in ~2 μsec. As the field strength grows the different groups of Rydberg states present are successively ionized, and the resulting

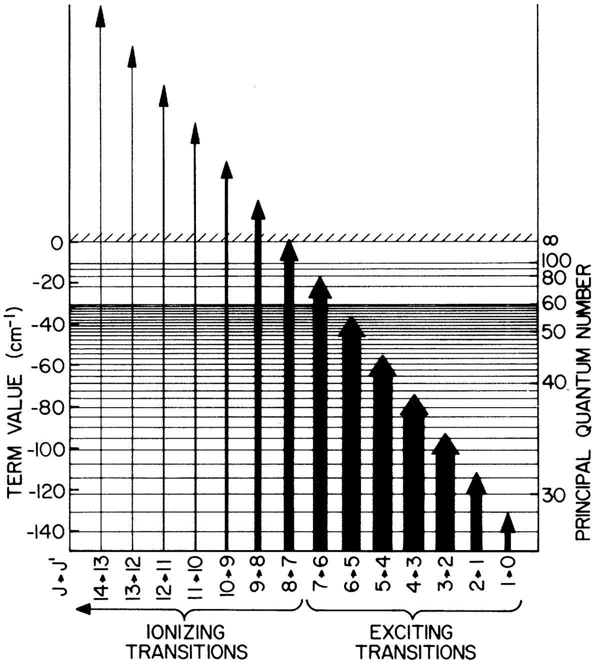

FIG. 1. Abbreviated term diagram for xenon showing effect of Xe(27f)-NH_3 collisions. The lengths of the arrows show the energies released in the NH_3 rotational de-excitations indicated. The widths of the arrows are proportional to the room-temperature populations of the upper rotational levels involved.

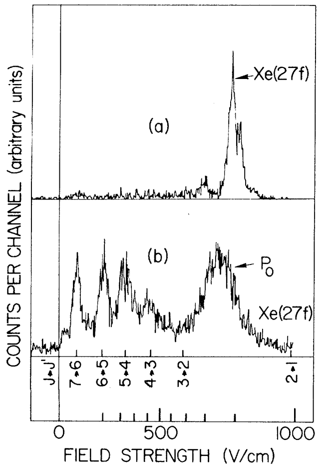

FIG. 2. Field-ionization signal as a function of ionizing field strength (a) without NH_3, (b) 10^{-5} Torr NH_3. Ionization field strengths obtained from Eq. (6) ($c = 10.1 \times 10^8$ V/cm) for the products of Reaction (4b) are indicated.

free electrons are swept into an electron multiplier. The electrons arising from different Rydberg states are thus resolved in time, and the arrival time of each electron can be easily related to the field strength at which it was liberated.

A time-to-amplitude converter (TAC) is started at the beginning of the ionizing voltage ramp and is stopped by the first electron pulse subsequently registered by the detector. The TAC output is fed into a standard multichannel pulse analyzer (MCA). For sufficiently low count rates (<1 per laser shot) the MCA output displays the probability of a field ionization event per unit time during the 2-μsec ramp. Measurement of the ionizing voltage wave form permits the determination of ionizing field strengths at which the ionization events occur.

Typical MCA outputs are shown in Figs. 2 and 3. For zero target-gas pressure a single peak [Fig. 2(a)] is observed corresponding to field ionization of the unmodified laser-excited Xe(27f) atoms. When $\sim 10^{-5}$ Torr NH_3 is introduced, spectra of the type shown in Figs. 2(b) and 3 are obtained. The most striking feature of these data is the series of well-defined peaks at low field strengths. These peaks explicitly demonstrate the occurrence of discrete energy transfer.

It is expected both theoretically[5] and experimentally[6] that the term values T_n' of the product Rydberg states are related to their critical field values E_n' by

$$E_n' \simeq cR^{-2}(T_n')^2, \qquad (5)$$

where R is the Rydberg constant. Combining Eqs. (3) and (5) yields

$$E_n' \simeq cR^{-2}(T_n + 2BJ)^2, \qquad (6)$$

where J is an integer in the range $0 \leq J \leq 7$.

Using Eq. (6) and the assumption that adjacent low-field peaks in Fig. 2(b) result from ionization of Rydberg states whose term values differ by $2B$, one can identify the peaks by determining those J assignments which, together with a fixed value for c, yield values for E_n' most consistent with the low-field peak positions in Figs. 2(b) and 3. The best fit of Eq. (6) with the data is obtained for a c value of 10.1×10^8 V/cm. The E_n' values with $c = 10 \times 10^8$ V/cm are shown in Figs. 2(b) and 3. Adopting the transition identifications shown, one can determine the principal quantum numbers of the product states. For example, the peak occurring at the lowest field in Fig. 2(b) is due to ionization of Xe($n \sim 75$) atoms formed by the reaction

$$\mathrm{Xe}(27f) + NH_3(J=7) \rightarrow \mathrm{Xe}(n \sim 75) + NH_3(J=6).$$

Several features of the data require explanation,

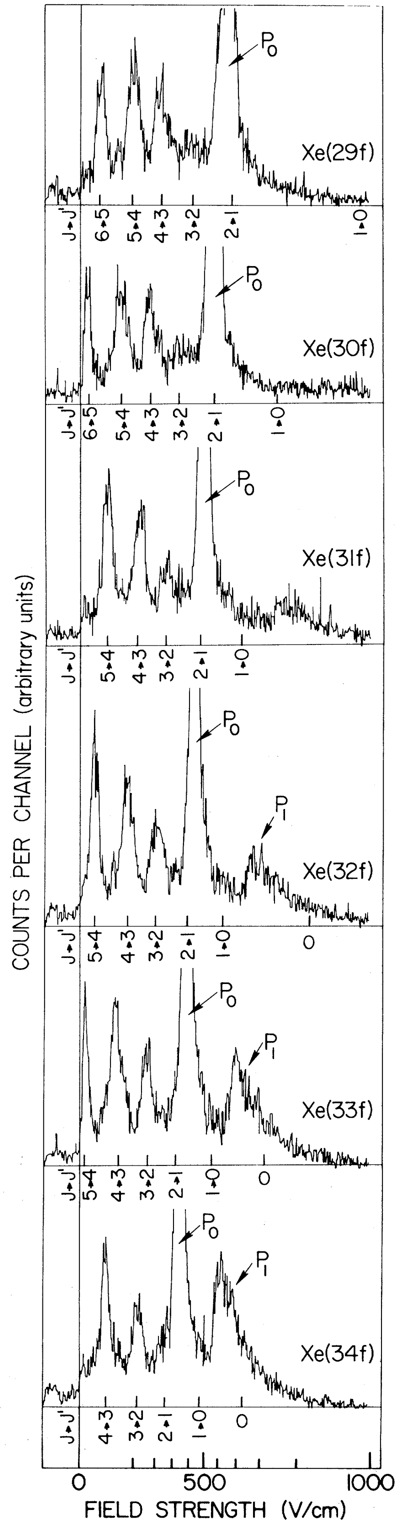

FIG. 3. Field ionization of products of Reaction (4b) for different initial values of n. Again, the peak positions obtained from Eq. (6) are noted. The position denoted "O" corresponds to collisions involving no change in J.

namely, (1) the absence of peaks associated with $J\to J-1$ transitions when $J<3$; (2) the absence in Fig. 2(b) of the narrow $27f$ peak and its replacement by the broader and displaced peak labeled P_0; (3) the fact that the $27f$ peak in Fig. 2(a) and the P_0 peaks in Figs. 2(b) and 3 do not consistently coincide with critical-field values given by Eq. (6) when $c=10.1\times10^8$ V/cm; (4) the appearance for $n\geqslant 31$ of an additional set of peaks labeled P_1 located on the high-field side of P_0.

Collisions involving low-lying rotational levels of NH_3 are expected to be infrequent because the population of these levels falls abruptly for $J<3$. Furthermore, such collisions tend to populate Rydberg states with $27\lesssim n\lesssim 40$ (Fig. 1). The density of states in this range of n is rather low and near-resonant transitions of the type (4b) are thus less likely than when the initial J values, and thus the final n values, are higher. As a consequence of these two effects the peaks associated with $J=2\to J=1$ and $J=1\to J=0$ transitions are small enough to be obscured by the larger peaks labeled P_0 and P_1. The broadening of P_0 in Fig. 2(b) with respect to the zero-pressure Xe($27f$) peak of Fig. 2(a) can be attributed to collisions of the type

$$\mathrm{Xe}(27jm_j)+\mathrm{NH}_3(J)\to\mathrm{Xe}(27j'm_j')+\mathrm{NH}_3(J), \qquad (7)$$

in which n and J are unchanged but the other quantum numbers may change. Collisions of this type have been reported recently by Gallagher, Edelstein, and Hill[7] for sodium Rydberg atoms incident on rare-gas atoms. Each of the product states has its own critical field, and the broad field-ionization peaks observed, P_0, correspond to a mixture of such product states.

The locations of the Xe($27f$) peak in Fig. 2(a) and the P_0 peaks in Figs. 2(b) and 3 are not consistent with the value for c (10.1×10^8 V/cm) obtained for the low-field peaks. This apparent paradox may be explained by the peaks labeled P_1 which emerge for $n>31$. In a subsidiary experiment it was observed that at a fixed value of n, the area of the P_1 peak grows relative to that of P_0 as the rate of change of ionizing field strength is increased. The fact that the magnitude of P_0 is slew-rate dependent points strongly to the conclusion that P_0 and P_1 both arise from Rydberg atoms of the same n and that the two peaks simply represent the outcomes of two different routes to ionization in a time-dependent electric field. Littman, Zimmerman, and Kleppner have observed[9] that the field-ionization characteristics of a particular level are often determined by the interaction of that level with more easily ionized levels. These interactions occur in the vicinity of avoided crossings between levels of the same $|m_l|$ belonging to manifolds of different principal quantum numbers. As noted by Gallagher *et al.*,[9] the details of the path taken to ionization depend on whether these avoided crossings are traversed diabatically or adiabatically. P_0 and P_1 are provisionally interpreted as resulting from ionization of products of Reaction (7) in processes occuring along predominantly adiabatic and diabatic paths, respectively. As shown in Fig. 3, the height of P_1 grows relative to P_0 as n increases. From this one might infer that the low-field (high-n) peaks are better characterized by diabatic ionization. It follows that the critical fields for the P_1 peaks should also be given by Eq. (6) with $c = 10.1\times 10^8$ V/cm. Inspection of Fig. 3 indeed shows that as n increases P_1 peaks become more fully developed and their location increasingly tends towards the series origin (i.e., E_n' for $J = 0$) of the low-field peaks. Thus with the exception of the P_0 peaks and the Xe(27f) peak in Fig. 2(a), the positions of all peaks are well represented by Eq. (6) with a c value of 10.1×10^8. The P_0 peaks and the Xe(27f) peak, on the other hand, result from adiabatic ionization and are thus characterized by a different value of c (in particular, 4.8×10^8 V/cm).

Thus in summation, all the data are consistent with the collision model outlined in the introduction in which rotational energy of NH_3 molecules is converted to electronic energy of Xe atoms. Similar results have been observed in this laboratory for ND_3 and HCl, and for these targets the product peak positions are correctly predicted by analysis similar to that applied to the NH_3 results. Rate constants for processes (4a) and (4b) have been estimated from the experimental observations. They are of order $10^{-6}-10^{-7}$ cm^3/sec, and tend to increase with increasing initial n level.

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