Charge transfer from molecular hydrogen to stored O^{2+} and O^{3+} ions

D. A. Church and H. M. Holzscheiter*
Department of Physics, Texas A&M University, College Station, Texas 77843
(Received 9 October 1987; revised manuscript received 29 March 1989)

The rate coefficients for charge transfer from H_2 molecules to O^{2+} and O^{3+} ions have been measured at eV energies using an ion-storage technique. A single rate coefficient $k(O^{3+},H_2)=(7.15\pm0.15)\times10^{-9}$ cm^3/s characterizes the O^{3+},H_2 interaction, but the attenuation of the stored O^{2+}-ion number due to charge transfer in a mixture of O_2 and H_2 gases exhibited a double time constant. Analysis employing the time dependence of the O^{2+}-ion metastable-level mean lives resulted in the charge-transfer rate coefficients $k(O^{2+}(^3P),H_2)=(1.71\pm0.15)\times10^{-9}$ cm^3/s and $k(O^{2+}(^1D),H_2)=(9.6\pm0.6)\times10^{-9}$ cm^3/s. The mean energy of the O^{2+} ions was 1.25(0.5) eV, while the O^{3+} ions were at 2.15(0.5) eV. The relationships to electron capture from H and from O_2 by these ions are discussed.

I. INTRODUCTION

Multicharged ions are common in both laboratory and astrophysical plasmas, and their rates of charge changing affect plasma properties such as resistivity, energy loss, and boundary conditions, etc., as well as providing means for analysis of plasma properties. Although the range of ion energies in such environments is extensive, particular theoretical interest centers on charge-changing collisions with atomic hydrogen at mean collision energies of a few eV or less. Such electron-transfer collisions with O^{q+} can be treated in a relatively straightforward manner as transitions occurring near avoided crossings between energy curves of the $(OH)^{q+}$ quasimolecule.[1] Nevertheless, extensive approximations in such quantum-mechanical calculations are commonly used, such as the neglect of angular couplings, and of electron translation factors, which are difficult to introduce in a general way, but which are essential for strict momentum conservation.[2] For certain final states of the system, it is argued that these approximations do not produce serious errors. However, theoretical comparisons of calculations with and without translation factors continue to be made, and experimental tests, although difficult, are desirable.

Measurements of charge-transfer cross sections for O^{2+} and O^{3+} ions colliding with both H_2 and H targets have been completed previously using an ion beam incident on the target gases in an oven capable of dissociating the H_2 molecule when heated.[3] The measurements were carried out at center-of-mass energies from 42.5 eV to 5 keV. An interesting feature of these ion-beam charge-transfer measurements was that the cross sections for capture by H and H_2 did not exhibit simple scaling laws, nor have uniform dependences on ion velocity,[13] although the cross sections were fairly close over the energy range investigated. This has also been found to be the case for measurements with other ions at comparable energies. However, for the $(OH)^{3+}$ quasimolecule calculations have been extended from below room temperature to 5 keV, and have been found to agree with the experimental results within 25% over the measured energy range.[4] The measurements reported here show that a relationship between H and H_2 cross sections may exist at the lowest energies. On the other hand, the charge changing between O^{2+} and O_2 is found to differ significantly from that between O^{2+} and H_2.

II. TECHNIQUE AND APPARATUS

Electron-transfer–rate coefficients are obtained using ion traps by determining the time constant for exponential loss of the stored ion number due to charge-changing collisions with a measured density of static target gas. The ions are produced in the trap by ionizing a (perhaps different) parent gas. The rate coefficient is calculated from the relationship $k=(n\tau)^{-1}$, where τ is the time constant for ion loss due to the target gas only. This time constant is conveniently found by performing measurements at different target-gas pressures, followed by a plot of the reciprocal of the measured ion-loss time constants τ_m versus target-gas density, yielding the rate coefficient from the slope.

A measurement method which relied on the appearance of the product ions from charge transfer would be complementary to this attenuation method. In cases where the product ions are stored in the trap, and hence observed, this, in fact, does supply additional important information.[5] However, the product ions from a multicharged-ion charge-transfer collision are both charged, and may have a repulsive potential energy at formation large compared to the typical mean stored ion energy. Such ions seem to be more rapidly lost from the trap, for reasons still only partially understood. However, this makes a quantitative use of product ions for charge-transfer measurements less desirable.

A second analysis method using the attenuation technique employs the density of the parent gas and the rate coefficient for electron capture by the parent ion in this gas. These quantities can be used with the density of the target gas to calculate the rate coefficient with the target gas from the measured loss time constant τ_m, i.e., $1/\tau_m=n_pk_p+n_tk_t$. Here, n_p and n_t are the parent- and

 ©1989 The American Physical Society

target-gas densities, and k_p and k_t are the rate coefficients for electron capture by the ions in the parent and target gases. The densities n_p and n_t are separately determined from the partial pressures in the trap. This latter measurement method requires more separate ion-storage measurements, but in the event of a nonexponential loss rate of the ions due to metastable ion states, it provides important information for the analysis of the more complex ion interactions.

Since it has been noted that very hot ions can be lost from the trap, and since an attenuation-measurement technique is used, it is important to verify that the ion sample under study is lost or changes charge only due to collisions. Although the properties under charge-changing conditions of the stored charge cloud in the trap are still a subject of study, they have been investigated by several types of measurements.

First, during and shortly after the $\approx$1-s electron-impact ionization interval, the ions approach an equilibrium temperature in the trap via ion-ion collisions.[6] The loss of hot ions from the top of the distribution in the axial potential well cools the remaining confined ions to a mean energy such that further ion loss by this mechanism is negligible.[7] It is still possible that ions may be lost radially, by diffusion across the magnetic field lines, if their canonical angular momentum is sufficiently large, or if a net torque is exerted on the ion cloud by ion-atom momentum-transfer collisions.[8] This loss mechanism has been studied in a Penning trap using stored electrons, which are nonreactive. The stored electron number remained constant in time until the distribution diffused to the radial trap electrode, at which time the stored number dropped smoothly toward zero over an extended time interval. This nonexponential loss rate was reduced as the confining magnetic field was increased. Thus, loss of ions by this mechanism would be apparent only at the lowest magnetic fields. Even for ions with low charge-transfer rate coefficients, this radial diffusion loss has not been identified during charge-transfer measurements at the typical magnetic fields employed.

Finally, there is by now considerable experience with calibration measurements using ion-neutral pairs having rates measured using other techniques, or in different types of traps, and comparisons with theoretical calculations, which all indicate that ion-storage measurements of charge-transfer–rate coefficients provide accurate results.

The apparatus used in these measurements did not differ significantly from that used earlier,[9] with the exception that a differentially pumped hydrogen source was added.[10] This source was only used as a gas-handling system for the introduction of H_2 during the measurements reported here. A valve connecting the source chamber to the ion-trap chamber was partially closed during measurements to prevent a H_2 beam from passing through the ion trap.

The Penning trap was operated in a magnetic field of approximately 0.8 T. At these fields, ion-storage times under typical conditions and at the base pressure of $\sim 10^{-10}$ Torr are in excess of 100 s for O^{2+}. Oxygen ions were produced by electron-impact ionization of O_2 gas introduced from a gas-handling system and maintained at a density of $4.8\times 10^7/\mathrm{cm}^3$. Typically, electron currents of a few μA in pulses of 1-s duration were used to produce convenient ion signals. Hydrogen gas was separately introduced through the source. The number density of H_2 molecules was obtained using the calibrated nude-ion-gauge reading, corrected for the gauge sensitivity for H_2 and for the calibration factor as determined with a capacitance manometer at pressures in the 10^{-3}–10^{-5}-Torr range. The accuracy of the calibration had previously been established by comparison of measured charge-transfer–rate coefficients with measurements made by other techniques.[9]

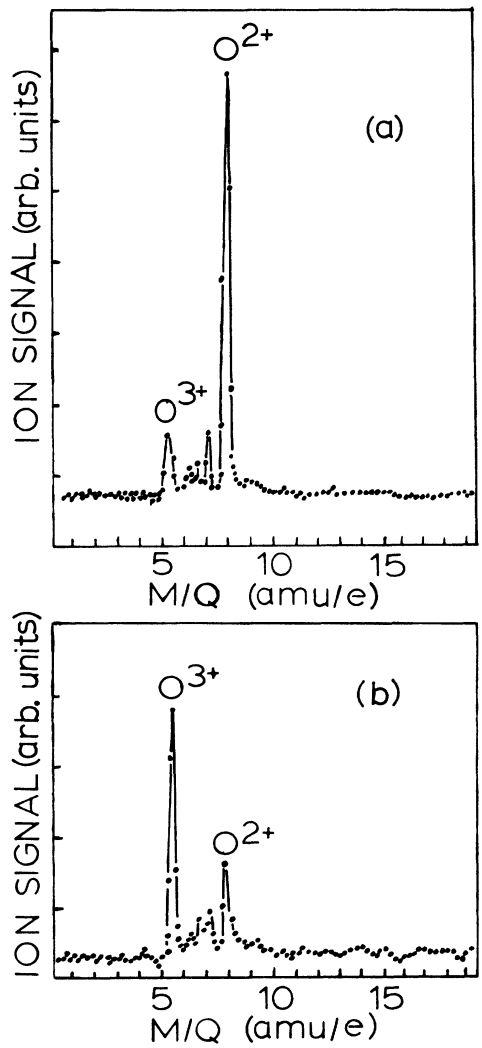

FIG. 1. Observed spectrum of ions in the Penning trap after resonant excitation for mass-to-charge ratios different from (a) O^{2+} or (b) O^{3+}.

The electric potentials of the trap, which established the mean ion energies, were the same as used in earlier measurements with oxygen ions.[10,11] All measurements were made with a single dominant charge state of the ions stored initially, e.g., during measurements on O^{2+}, the other ion types including O^{3+} were largely driven from the trap by swept, resonant excitation at the cyclotron frequency during the ionization pulse as shown in Fig. 1.

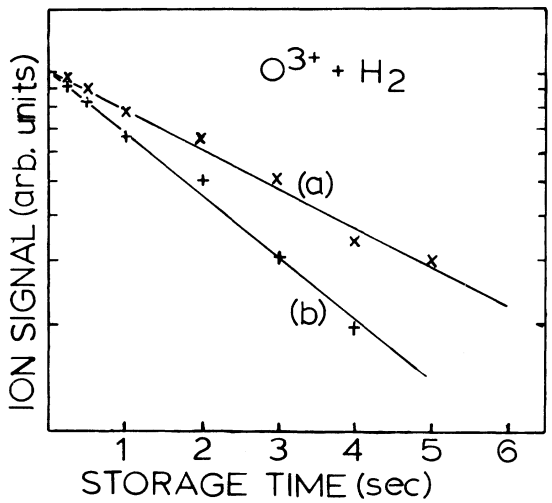

FIG. 2. Ion signal vs reaction time for O^{3+} ions reacting with H_2 at target densities of (a) $n = 1.83\times10^7$ cm^3 and (b) $n = 3.66\times10^7$ cm^3.

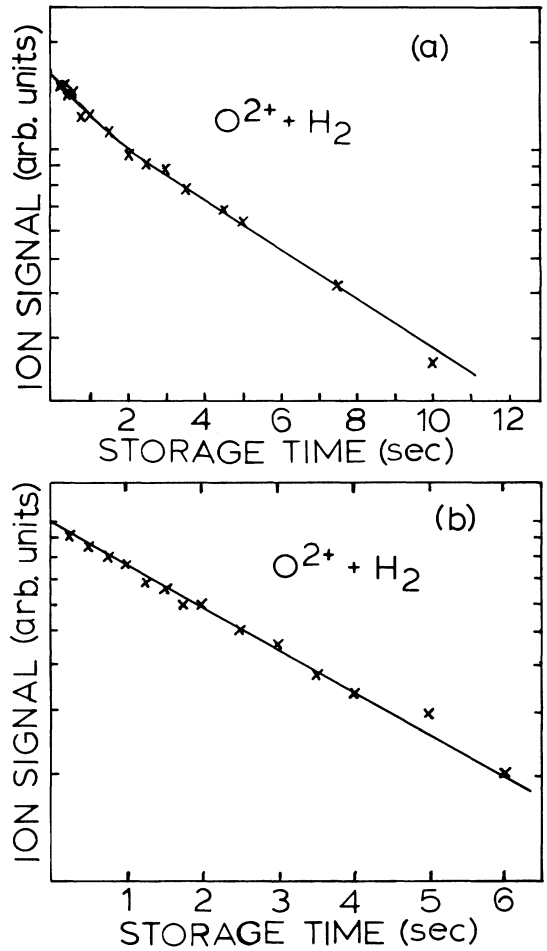

FIG. 3. Ion signal vs storage time for O^{2+} ions reacting with H_2. (a) At electron-impact energies of 400 eV a double-exponential decay curve resulting from population of the metastable ^1D state is observed. (b) At 76 eV impact energy the population of the ^1D state is negligible, and the ion decay exhibits a single-exponential behavior.

III. MEASUREMENTS

Initial measurements using both O^{2+} and O^{3+} were carried out using 400-eV-energy electrons to produce the multicharged-ion states. The O^{3+} measurements made at several pressures of H_2 in the 10^{-9}-Torr range exhibited a single-exponential decay of the stored ion number with interaction time (see Fig. 2). The O^{2+}-ion decay had a nonexponential behavior, as shown in Fig. 3(a). This second type of ion loss is associated with the presence of long-lived metastable levels of the O^{2+} ions, in addition to the $2p^2\,{}^3P$ ground state. The possibilities include the $2p^2\,{}^1S$ level, which has a calculated mean lifetime of 0.55 s, and the $2p^2\,{}^1D$ multiplet, which has a calculated mean lifetime near 37 s. The O^{2+}-ion loss curves were least-squares fitted to a sum of exponentials. The fitted parameters were the initial ion numbers and the decay constants of the exponentials. The smallest value of the parameter quantifying the fit was obtained for a two-exponential rather than a three-exponential decay, e.g., $N(t) = N_{01}e^{-t/\tau_1}N_{02}e^{-t/\tau_2}$. Both of the time constants τ_1, τ_2 were found to be longer than the mean lifetime of the ^1S level. Actually, the measurements discriminated against observation of the ^1S level, which should have effects only at time intervals ≤ 0.5 s.

To determine which of the two exponentials correspond to the $O^{2+}(^3P)$ ground state, measurements were performed in which the ions were produced with electrons having 70 eV energy. The rate of production of metastable levels is lower with reduced ionizing electron energy. With the 70-eV electrons, stored-ion decays which appeared to be single exponentials were obtained, as Fig. 3(b) shows. When least-squares fitted to single and double exponentials, the single exponential provided by far the best fit. In Fig. 4 the reciprocals of the measured time constants are plotted versus the H_2 molecule density and compared with the data obtained using 400-eV electrons. This shows clearly that the longer-time-

TABLE I. Summary of results for the reactions $O^{3+} + H_2$, $O^{2+}(^3P) + H_2$, and $O^{2+}(^1D) + H_2$ obtained with the different methods described in the text.

Reaction	$k(10^{-9}$ cm^3/s) from direct fit of data to $1/\tau = 1/\tau_2 + nk$	$k(10^{-9}$ cm^3/s) from raw data corrected for known loss mechanisms	Average result $k(10^{-9}$ cm^3/s)
$O^{3+} + H_2$	$k = 7.13\pm0.13$	$k = 7.2\pm0.15$	7.15 ± 0.15
$O^{2+}(^3P) + H_2$	$k = 1.65\pm0.15$	$k = 1.78\pm0.15$	1.71 ± 0.15
$O^{2+}(^1D) + H_2$		$k = 9.6\pm0.6$	9.6 ± 0.6

constant ion-loss rate was associated with the ^3P ground state, leaving the ^1D multiplet as the source of the faster rate of ion loss. At this point, it should be recalled that the loss rate of O^{2+} ions in O_2 gas is characterized by a single exponential,[11] which indicates that the ^1D and ^3P states change charge at the same rate in that gas. The increased loss rate of the $O^{2+}(^1D)$ ions is characteristic of the H_2 target.

The rate coefficient for the ^3P state of O^{2+} in H_2 was determined by each of the two methods discussed in Sec. II. The densities of H_2 at the various measurement pressures were calculated, and the rate coefficient was computed from the relation $k=(n\tau)^{-1}$. The value of τ was obtained from the measured time constant τ_{in} by correcting for the measured loss time constant for O^{2+} ions in O_2 alone, τ_2, using the relation $1/\tau=1/\tau_m-1/\tau_2$. The result is $k(O^{2+}(^3P),H_2)=1.78\times10^{-9}$ cm^3/s. Alternatively, the slope of the plot of the $1/\tau_m$ versus $n(H_2)$, as shown in Fig. 4, was calculated, yielding $k(O^{2+}(^3P),H_2)=(1.65\pm0.15)\times10^{-9}$ cm^3/s. The intercept of this curve (Fig. 4), in general, corresponds to the rate for loss of ions to other target gases, and reproduces the independently measured rate constant for O^{2+} on O_2 as expected, since the densities of residual gases were negligible.

The time constant for loss by charge changing of the ions in the ^1D state requires correction for both charge changing with O_2, and for the radiative reduction of the population during the measurement with time constant τ_R. Of course, radiative depletion of the ^1D ions augments the ^3P-ion population, but the fact that the rate is so low, coupled with the smaller ^1D population, produces a correction to the ^3P time constant which is negligible compared to statistical uncertainties. However, for the ^1D state, $1/\tau(^1D)=1/\tau_m-1/\tau_2-1/\tau_R$, and $k(O^{2+}(^1D),H_2)=(9.6\pm0.6)\times10^{-9}$ cm^3/s provides the corrected result.

Analysis of the O^{3+} data in similar ways yields $k(O^{3+},H_2)=(7.2\pm0.15)\times10^{-9}$ cm^3/s using the measured time constant corrected for ion loss due to $O^{3+}+O_2$ reactions, and the density of the H_2 gas. Direct analysis of the measured time-constant dependence on the target-gas density (Fig. 5) yields a rate constant $k(O^{3+},H_2)=(7.13\pm0.13)\times10^{-9}$ cm^3/s from the slope. A time constant for the reaction of O^{3+} with the O_2 gas, at the O_2 density used, of $\tau=7.6$ s obtained from the intercept is in excellent agreement with the values obtained by the first method. The results are summarized in Table I. In addition to the statistical errors given, there is the possibility of a systematic error due to the pressure calibration, which can be in the order of up to 30% at the lowest pressures.

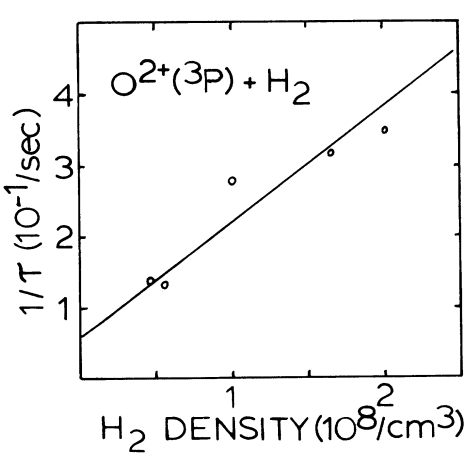

FIG. 4. Decay time constants $1/\tau$ vs H_2 density for the reaction $O^{2+}(^3P)+H_2$. The solid line is a least-squares fit to the experimental data. The intercept reproduces the independently measured time constant for the reaction $O^{2+}+O_2$.

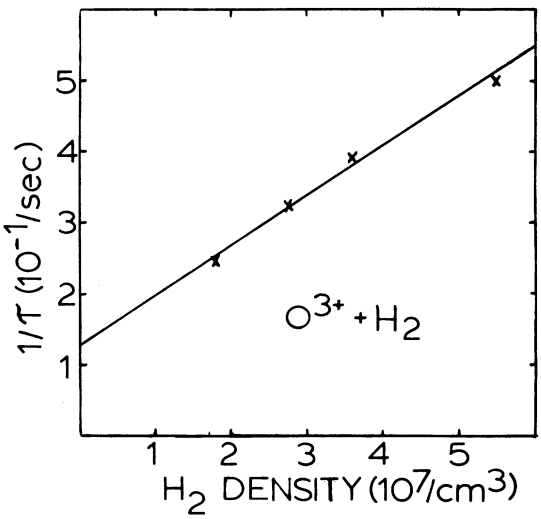

FIG. 5. Decay time constants at different gas densities for the reaction $O^{3+}+H_2$.

IV. DISCUSSION

The possibility of heavy-particle transfer exists in low-energy reactive collisions of singly charged ions with molecules. Such reactions are not always energetically forbidden to multicharged ions, but the charge-changing collisions of multicharged ions are theoretically analyzed in terms of the highly probable electron-transfer reactions. Only electron-transfer interpretations of the data are discussed here.

There are currently no quantum-mechanical calculations for the rate coefficients for electron capture by two- or three-times-ionized oxygen ions from H_2 at the lowest energies, although calculations for $(OH)^{2+}$ and $(OH)^{3+}$ collisions[1,12] and for bound states of these molecular ions[13] have been completed. The Langevin rates are $k_L(O^{2+},H_2)=3.1\times10^{-9}$ cm^3/s and $k_L(O^{3+},H_2)=4.7\times10^{-9}$ cm^3/s. One sees that the measured O^{3+},H_2 rate is 50% above the Langevin rate.

By analogy with the recent model-potential calculations by Gargaud and McCarroll[14] for several ions on H_2, one might expect that the O^{q+},H_2 collisions will be similar to the O^{q+},H collisions, with the potential surface crossings shifted to larger radius by the 1.8-eV-higher ionization potential of H_2. At the lowest collision ener-

gies, appropriate here, the cross sections obtained by Gargaud and McCarroll for $(NH)^{3+}$ and $(NH_2)^{3+}$ were found to be nearly identical. The calculated ground-state rates for collisions with H are $k(O^{2+},H)=1.2\times10^{-9}$ cm^3/s and $k(O^{3+},H)=8\times10^{-9}$ cm^3/s at the measurement energies[1,12] the latter result being very close to our measurement value for O^{3+},H_2.

The relatively low rate coefficient for O^{2+} electron capture from H is a consequence of the necessity for core rearrangement of the O^{2+} electrons in order for capture to occur. The reaction is $O^{2+}(2s^22p^2\,{}^3P)+H\rightarrow O^+(2s2p^4\,{}^4P)+H^+$ for the lower ${}^4\Pi$ and ${}^4\Sigma^-$ states of the $(OH)^{2+}$ quasimolecule. The diabatic curve crossings occur only if one of the oxygen s electrons is promoted to the $2p$ state during the capture collision. This is accompanied by a sign change in the coupling matrix elements to the ${}^4\Sigma^-$ curve which reduces the charge-transfer probability.[1,12] On the other hand, there are numerous curve crossings and no rearrangement is necessary for the O^{3+},H charge-transfer collisions, leading to a high probability of the electron capture.

The ratio of the theoretical values $k(O^{3+},H)/k(O^{2+},H)=6.7$, while the ratio of the experimental values $k(O^{3+},H_2)/k(O^{2+}(^3P),H_2)=4.1$. The H_2 target clearly behaves in a similar manner to the H target in the sense that both ratios are large. For $(OH_2)^{3+}$ one can then expect that numerous curve crossings occur, while for $(OH_2)^{2+}$ electron transfer at some curve crossings may well involve some core rearrangement of the oxygen electrons, since the rate coefficient falls below the Langevin value. However, it has already been noted that at the higher collision energies the trend of the experimental magnitudes of the cross sections for charge transfer from H_2 and from H show no particular relationship[3] for either O^{2+} or O^{3+}. The reason for this behavior, in view of the similarities of the rates at the lowest energies noted in collisions of H_2 and H with nitrogen ions,[15] is the opening of additional reaction channels as the ion energies are increased.

By way of contrast, the low-energy rates for O^{2+},H_2 and O^{2+},O_2 collisions differ significantly. The electron-transfer rate from O_2 is low, and is the same for the ${}^3P$ and ${}^1D$ multiplets. The rate for the $O^{2+}(^3P),H_2$ collision is larger by a factor of 1.8, and $k(O^{2+}(^1D),H_2)$ exceeds even the O^{3+},H rate coefficient. Thus differences in the crossings of the potential-energy surfaces in these collisions are decisive in determining the magnitudes of the rate coefficients for electron capture.

Finally, it should be noted that, in cases when the electron-transfer rate of a metastable excited state differs from that of the ground state, this measurement technique could be used to obtain the metastable-level mean lifetime. Since the time constant for the rate of loss of the metastable ions depends both on the target-gas pressure and on the mean lifetime of the level, measurements in which the target-gas pressure is varied, and hence in which the measured ion-loss rate is changed, should yield sufficient information to obtain the radiative decay constant. In the case of the $O^{2+}(^1D)$ state discussed here, this was not possible, due to the disparity in the charge transfer and radiative time constants.

ACKNOWLEDGMENTS

This research was supported by the Robert A. Welch Foundation, as well as by the U.S. National Science Foundation and the Texas A&M Center for Energy and Mineral Resources.

---

*Present address: Los Alamos National Laboratory, Los Alamos, NM 87545.

[1]A. Dalgarno, T. G. Heil, and S. E. Butler, Astrophys. J. **245**, 793 (1981).
[2]J. B. Delos, Rev. Mod. Phys. **53**, 287 (1981).
[3]R. A. Phaneuf, I. Alvarez, F. W. Meyer, and D. H. Crandall, Phys. Rev. A **26**, 1892 (1982).
[4]S. Bienstock, T. G. Heil, and A. Dalgarno, Phys. Rev. A **27**, 2741 (1983).
[5]D. A. Church and H. M. Holzscheiter, Chem. Phys. Lett. **76**, 109 (1980).
[6]D. A. Church, Phys. Rev. A **37**, 277 (1988).
[7]D. A. Church and H. G. Dehmelt, J. Appl. Phys. **40**, 3127 (1969).
[8]T. S. Grassie and J. H. Malmberg, Phys. Fluids **23**, 63 (1980).
[9]H. M. Holzscheiter and D. A. Church, J. Chem. Phys. **74**, 2313 (1981).
[10]D. A. Church and H. M. Holzscheiter, Phys. Rev. Lett. **49**, 643 (1982).
[11]H. M. Holzscheiter and D. A. Church, Phys. Lett. **86A**, 25 (1981).
[12]T. G. Heil, S. E. Butler, and A. Dalgarno, Phys. Rev. A **27**, 2365 (1983).
[13]S. Preston and A. Dalgarno, Chem. Phys. Lett. **138**, 157 (1987).
[14]M. Gargaud and R. McCarroll, J. Phys. B **18**, 463 (1985).
[15]H. -Y. Wang and D. A. Church, Phys. Rev. **36**, 4261 (1987).