Lifetime of the $c\,^3\Pi_u$ Metastable State of H_2, D_2, and HD†

Charles E. Johnson
Department of Physics and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720
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The lifetime of the $v=0$ $c\,^3\Pi_u$ metastable state of H_2, D_2, and HD has been measured using the time-of-flight technique. The velocity distribution of a thermal beam of metastable molecules is sampled and detected at two positions, 1.9 and 6.7 m from the pulsed electron gun used to excite the ground-state molecules effusing from a source slit. A comparison of the number of metastables within specific velocity intervals at the two detectors determines the number which decay in flight and yields an experimental plot of the number which decay versus time of flight. The lifetime τ is then obtained from the slope $(=-1/\tau)$ of a straight line least-squares fitted to the decay plot. The result, $\tau = 1.02 \pm 0.05$ msec, is the same for both para- and ortho-H_2, as well as for D_2 and HD. Since all three isotopic combinations have the same measured lifetime, and since the lifetime for a forbidden predissociation through spin-orbit mixing with the $^3\Sigma_u^+$ state would be expected to depend upon details of the fine structure, our value is the radiative lifetime for a combination of magnetic-dipole electric-quadrupole decay of the $v=0$ $^3\Pi_u$ state to the repulsive $^3\Sigma_u^+$ state.

I. INTRODUCTION

The time-of-flight technique previously employed to measure the two-photon radiative lifetime[1] of the $2\,^1S_0$ metastable state of He has been used to investigate the lifetime of the $c\,^3\Pi_u$ metastable state of H_2, D_2, and HD.[2] The $c\,^3\Pi_u$ state, first shown to be metastable by Lichten,[3] is the only metastable state of the hydrogen molecule, and its lifetime is of fundamental interest because H_2 is one of the simplest molecular systems. Furthermore, knowledge of the metastable state lifetime is useful in connection with the formation of an energetic neutral hydrogen beam[4] for injection in controlled thermonuclear experiments and in understanding the loss processes occurring in the hydrogen plasma.

The original experiment of Lichten on the fine structure of the $N=2$ rotational level of para-hydrogen[3,5]—later extended to include the fine and hyperfine structure of the $N=1$ rotational level of ortho-hydrogen[6]—implied a lower limit of about 50 μsec for the lifetime, since this was approximately the time of flight of the metastable molecules through his molecular-beam magnetic-resonance apparatus. Subsequent preliminary measurements, using the molecular-beam magnetic-resonance apparatus as a state selector, indicated that the lifetime varied from 0.1 to 0.5 msec among different fine-structure levels[7]; a forbidden predissociation into the repulsive $^3\Sigma_u^+$ state was postulated to explain the experimental results.[7,8] The competing decay mode of a magnetic-dipole electric-quadrupole transition to the same $^3\Sigma_u^+$ state has been estimated to result in a lifetime of about 1 msec for the $c\,^3\Pi_u$ state.[9]

Following a discussion of the metastability of the various vibrational-rotational levels of the $c\,^3\Pi_u$ state, this paper outlines the time-of-flight technique and apparatus, and then explains the data analysis used to obtain an experimental result for the lifetime of the $c\,^3\Pi_u$ metastable state of H_2, D_2, and HD.

II. $c\,^3\Pi_u$ METASTABLE LEVELS

The $c\,^3\Pi_u$ state, approximately 12 eV above the ground state (see Fig. 1), cannot decay by an electric-dipole transition to either the $^1\Sigma_g^+$ ground state or the lower-lying repulsive $^3\Sigma_u^+$ state; a transition

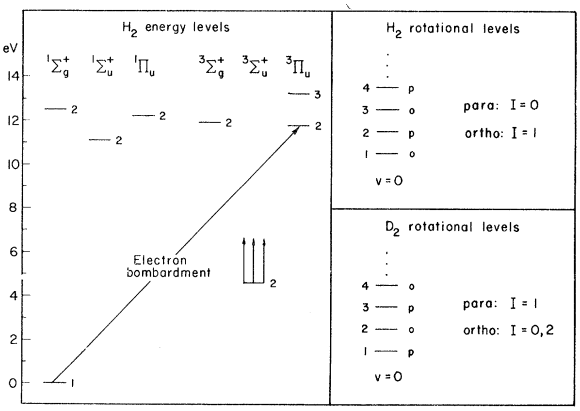

FIG. 1. H_2 energy-level diagram showing the lowest-lying levels. The $c\,^3\Pi_u$ metastable state is produced by electron bombardment. Its decay to the $^3\Sigma_u^+$ state occurs by a combination of magnetic-dipole electric-quadrupole decay. As shown on the right, only half of the rotational levels are metastable: odd rotational levels of ortho-H_2 and para-D_2, and even rotational levels of para-H_2 and ortho-D_2. The other half decay by allowed predissociation through mixing with the repulsive $^3\Sigma_u^+$ state.

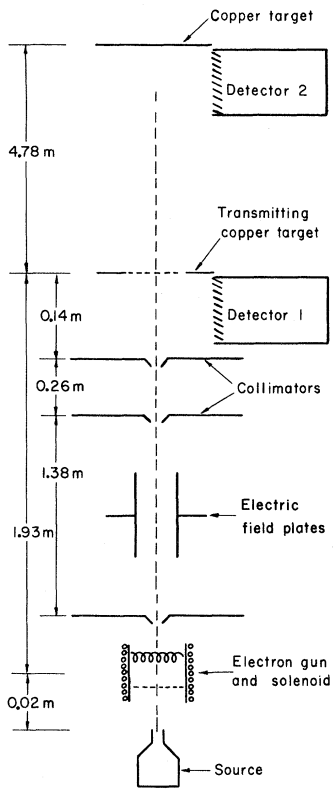

FIG. 2. Apparatus outline. Ground-state molecules effuse from the source slit and are excited to the $c\,^3\Pi_u$ metastable state by electron bombardment. Hydrogen atoms in the $2\,^2S_{1/2}$ metastable state are quenched by the electric field. The metastable molecules are detected at both ends of the time-of-flight region.

to the $^1\Sigma_g^+$ state would violate the spin selection rule $\Delta S = 0$, which holds quite well for Hund's case (b), while a transition to the $^3\Sigma_u^+$ state would violate the general selection rule $g \nleftrightarrow u$ for a molecule with nuclei of equal charge.[10] However, in this experiment only the $v = 0$ vibrational level can be considered as being metastable. The $v = 1$ level lies above the lowest levels of the $^3\Sigma_g^+$ state, and consequently the higher vibrational levels of the $^3\Pi_u$ state decay by electric-dipole emission to the $^3\Sigma_g^+$ state. The calculated radiative lifetime[9] for those $^3\Pi_u$ vibrational levels higher than $v = 0$ is approximately 0.1 msec and is too short compared to the time of flight in our apparatus to allow these higher vibrational levels to be detected.

Another possible decay mode for the $c\,^3\Pi_u$ state is that of allowed predissociation induced by rotational-electronic perturbations mixing the $^3\Pi_u$ state with the repulsive $^3\Sigma_u^+$ state; the lifetime for this allowed predissociation is less than 0.3 μsec.[11] But an examination of the Krönig selection rules indicates that only half of the $v = 0$ $^3\Pi_u$ rotational levels have the correct symmetry to decay by this allowed predissociation.[12] As shown in Fig. 1, the remaining half of the $^3\Pi_u$ rotational levels—the metastable levels—are the odd rotational levels of ortho-H_2 and para-D_2, and the even rotational levels of para-H_2 and ortho-D_2. A similar situation holds for HD, except that the ortho-para designation is lost.

The metastable half of the $v = 0$ $^3\Pi_u$ rotational levels can decay by either a combined magnetic-dipole electric-quadrupole transition to the repulsive $^3\Sigma_u^+$ state or possibly by a forbidden predissociation through spin-orbit mixing with the same $^3\Sigma_u^+$ state. The forbidden predissociation decay was postulated to explain an observed variation of the lifetime among different fine-structure levels[7,8]; the magnetic-dipole electric-quadrupole radiative lifetime,[9] estimated to be about 1 msec, should be independent of the particular level.[8] Therefore the measured lifetime should be the same for both para- and ortho-H_2, and perhaps also for D_2 and HD, if the metastable components in our beam decay by a combined magnetic-dipole electric-quadrupole emission, while a forbidden predissociation decay would give a different measured lifetime for the three isotopic combinations.

III. EXPERIMENT

A complete description of our apparatus and data-collection scheme has been reported previously.[1] For the present investigation of the $c\,^3\Pi_u$ metastable state of H_2, D_2, and HD, electric field plates have replaced the resonance quenching lamp used in our earlier experiment on the $2\,^1S_0$ metastable state of He (see Fig. 2). An electric field of about 500 V/cm quenches H atoms in the $2\,^2S_{1/2}$ metastable state,[13] eliminating them from our metastable beam, but has no observable effect on the $^3\Pi_u$ metastable molecules.[14] The only other changes are related to the particular source gas. For D_2 and ortho-H_2, a Pd leak served not only to control the gas flow from the storage tank but also to eliminate impurities, mostly N_2, from the gas. For para-H_2, the process[15] of converting the room-temperature ortho-para mixture into pure para-H_2 through contact with a catalyst at low temperature (~20 K) also removed any impurities by freezing; a needle valve controlled the flow rate of evaporating para-H_2 into the source line from the low temperature region. And for HD, a low temperature (~25 K) trap in the source line purified the gas after the needle valve.

Although H_2 is $\frac{3}{4}$ ortho and $\frac{1}{4}$ para at room temperature (300 K), this mixture can be considered to be entirely ortho-H_2 for this lifetime measurement. Since ortho-D_2 is the form obtained at low temperature, instead of para as for H_2, there is little advantage in converting to pure ortho-D_2 at low temperature because room-temperature D_2 is

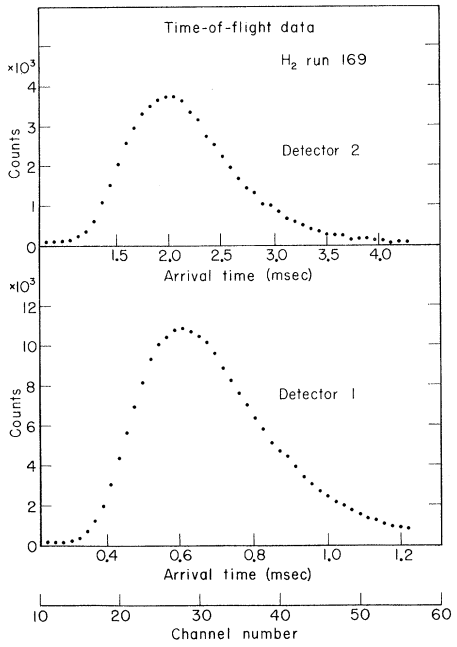

FIG. 3. Time-of-flight distributions, representing about 10^6 separate collection sweeps. The channel numbers are for detector 1; the data points for detector 2 have been partitioned and averaged over velocity intervals whose width is determined by the channel width at detector 1.

already $\frac{2}{3}$ ortho. Therefore a separate measurement of the $^3\Pi_u$ lifetime is possible for both para- and ortho-H_2, but is impractical for D_2. A brief summary is now given of those aspects of the experiment which are pertinent to understanding the present investigation.

The experiment is based on the time-of-flight technique where an atom or molecule is assumed to leave the metastable state only by radiative decay as it drifts over a 5-m path between two fixed detectors; this assumption demands a very low pressure ($< 10^{-7}$ Torr) in the drift region to minimize scattering losses. As shown in Fig. 2, the neutral ground-state beam effuses from a source slit; the molecules are immediately excited to metastable states by a pulse of antiparallel magnetically focused electrons. The metastable beam is then collimated while passing through three buffer chambers and finally detected at both ends of the 5-m drift region. The first detector consists of a 60% transmitting copper mesh target. The secondary electrons which are ejected from the copper surface by the metastable molecules are collected by an EMI electron multiplier. The second detector is a solid copper target and intercepts the transmitted metastable molecules which survive the flight between the two detectors.

The data-taking and timing aspects of the experiment are controlled by an on-line PDP-8 computer. An example of the data collected is shown in Fig. 3, and represents about 10^6 separate collection sweeps during a total collection time of 8 h. The electron gun is pulsed on only during channel 0 and counts are then collected simultaneously at both detectors into 199 channels, not all of which are shown. All channel widths are equal to 21.75 μsec. The time-of-flight distribution at detector 2 has been integrated over a partition width which corresponds to the channel width at detector 1 for metastable molecules with the same velocity. The amount of background subtraction is obtained from the long tail of the detector-1 time-of-flight distribution, and from the beginning few channels of the detector-2 distribution.

IV. ANALYSIS

The time-of-flight technique is ideally suited for a lifetime measurement only when the beam consists of a single metastable state. Otherwise it is usually necessary to interpret the experimentally measured decay as an "average" lifetime of the metastable states in the beam. Even though the initial excitation of the beam may simultaneously yield several metastable states, a metastable beam containing a single state can sometimes be obtained by using state-selecting techniques such as resonance quenching[1] or molecular-beam resonance.[7] Although the excitation of H_2, D_2, and HD may produce several rotational metastable states, our low count rate makes state selection very impractical. Consequently, to avoid the "average" lifetime interpretation, our experimental data must be analyzed to determine if states with different decay rates are present in the beam.[16]

A. Experimental Decay Plot

The experimental plot of the number of metastable molecules which decay versus time of flight is obtained from the distributions shown in Fig. 3. The correct partitioning of the detector-2 distribution assures that each point for both detectors corresponds to metastable molecules with the same velocity. Then the ratio R of detector-2 to detector-1 data is taken; the natural logarithm of this ratio versus time of flight t is our decay plot.

If only one component were present, as in our previous discussion[1] of the time-of-flight technique, $\ln R$ vs t would be a straight line, and the lifetime τ of the metastable state would be obtained from the slope ($= -1/\tau$) of this straight line. But since we expect several rotational levels of the $c\,^3\Pi_u$ state to be metastable and to possibly have different radiative lifetimes, we must now explicitly consider this possibility.

B. Theoretical Decay Plot

The number of molecules in a particular meta-

stable state k with initial velocity distribution $n_0(v,k)$, which arrive at detector i at time t_i, is $n_0(v,k)e^{-t_i/\tau_k}$; the exponential factor allows for the possibility of radiative decay with mean life τ_k. The probability of detecting a particular metastable molecule depends upon the surface efficiency $\epsilon_i(k)$ of detector i. Although this efficiency should be velocity independent for the thermal velocity range of this experiment, it is not necessarily true that the efficiency is independent of position on the detector surface. The total number $N_i(v)$ of metastable molecules with velocity v that are counted at detector i is therefore obtained not only by summing over the different metastable states k, but also by integrating over the surface of the detector:

$$N_i(v) = \sum_k \int_{\text{surface}} \epsilon_i(k)\, n_0(v,k)\, e^{-t_i/\tau_k}\, dS . \qquad (1)$$

Dependence on the details of the detector surface is eliminated by ensuring that the initial velocity distribution $n_0(v,k)$ is uniform across the beam so that each position on the detector surface sees the same velocity distribution. The number of metastable molecules counted is then

$$N_i(v) = \sum_k C_i(k)\, n_0(v,k)\, e^{-t_i/\tau_k} , \qquad (2)$$

where $C_i(k) = \int_S \epsilon_i(k)\, dS$ is a constant efficiency factor of the ith detector. The ratio of the number of metastable molecules in the same velocity interval at two spatially separated detectors yields the desired decay plot, since, with the reasonable assumption that the efficiency factor $C_i(k)$ is the same for all states k, the ratio

$$R = \frac{N_2(v)}{N_1(v)} = C\,\frac{\sum_k n_0(v,k) e^{-t_2/\tau_k}}{\sum_k n_0(v,k) e^{-t_1/\tau_k}} \qquad (3)$$

is independent of the two detector efficiencies except for an over-all normalization constant C. Moreover, the initial velocity distribution, determined not only by the effusion from the source slit but also by the excitation process in the electron gun, is the same for all states k; therefore the ratio R is also independent of the initial velocity distribution.

If all the metastable states in the beam decay at the same rate $\tau_k \equiv \tau$, then Eq. (3) reduces to

$$R = Ce^{-t/\tau}, \qquad (4)$$

which is identical to the result for a single metastable component. Thus $\ln R$ versus time of flight $t = (t_2 - t_1)$ is a straight line whose slope $(= -1/\tau)$ yields the lifetime τ. However, if the metastable states have different decay rates, then $\ln R$ vs t is no longer a straight line.[16] Therefore, a comparison of the slope of the first half of our experimental decay plot with that of the second half serves as a simple, but effective, test for curvature; any curvature indicates that metastable states with different decay rates are present in the beam.

Additional information about our ability to experimentally observe different decay rates is obtained by examining the predictions of Eq. (3) for a beam containing just two components. If the two components have an initial relative population ratio $R_{21} = n_0(2)/n_0(1)$, then Eq. (3) becomes

$$R = \frac{e^{(-D_2/D)(t/\tau_1)} + R_{21}\, e^{(-D_2/D)(t/\tau_2)}}{e^{(-D_1/D)(t/\tau_2)} + R_{21}\, e^{(-D_1/D)(t/\tau_2)}} , \qquad (5)$$

where $D_1 = vt_1$ is the distance to the first detector, $D_2 = vt_2$ the distance to the second detector, and $D = D_2 - D_1 = vt$ the distance between the two detectors. A predicted decay plot of $\ln R$ vs t using Eq. (5), when compared to one using Eq. (4), serves to furnish limits for τ_1 and τ_2 such that curvature is detectable.

An absolute lower limit for the lifetime of any detectable metastable component is provided by the apparatus itself, since even the fastest metastable molecules require at least 0.4 msec to arrive at the first detector (see Fig. 3). Thus, to be measurable, the lifetime of any metastable state must be greater than about 0.5 msec, and any decay mode giving a shorter lifetime is unimportant for our experiment.

V. RESULTS

A. Errors

Compared to other sources of error, the statistical error is sufficiently small that it does not contribute to the final error. The first significant error arises from a systematic source position effect previously discussed in detail[1]; this systematic error is due to the initial velocity distribution $n_0(v)$ being slightly nonuniform across the metastable beam. Another systematic error occurs because the electron bombardment region extends for 1 cm along the atomic beam direction. This leads to an uncertainty in the velocity interval over which the detector-2 distribution is integrated, since the finite bombardment region results in an uncertainty in the effective distance to the two detectors. The combination of these two systematic errors contributes about half to the final error of 0.05 msec.

The remaining half of the final error results from an uncertainty in the amount of background subtraction at detector 2. In the present experiment the peak count rate—approximately equal for all three isotopic combinations—is much lower than, for example, in our lifetime measurements on the metastable states of either He, CO, or the noble gases.[1,16,17] Consequently, the background at detector 2 is an appreciable fraction, about 10%, of the peak value. The error in the determination of this background from the beginning few channels leads to a significant error in the lifetime result.

Finally, we mention that, except for the two

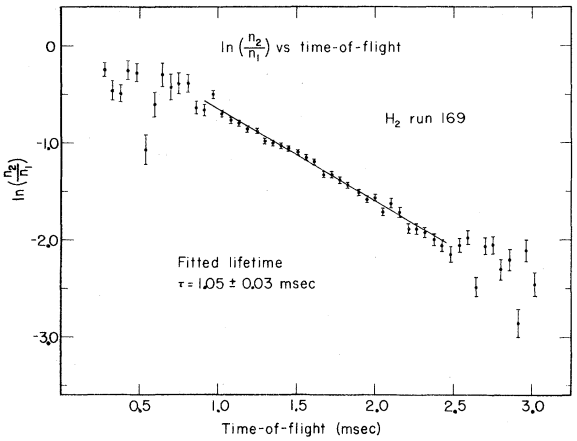

FIG. 4. Decay plot. The ratio of detector-2 to detector-1 metastable molecule distributions versus time of flight between detectors is a straight line on a logarithmic plot. The measured lifetime τ is obtained from the slope ($=-1/\tau$) of the least-squares-fitted straight line, using data points corresponding to a number of counts greater than 10% of the peak value.

systematic effects already discussed, all other experimental parameters such as electron gun voltage, source temperature, channel width, beam flow rate, and drift region pressure have no effect on the measured lifetime.

B. $c\,^3\Pi_u$

There is no evidence for any of our runs on either H_2, D_2, or HD that the metastable states in the beam decay at other than a single uniform rate. For one component with a lifetime τ of 1.0 msec, a comparison of the two-component prediction of Eq. (5) with the single-component fit of Eq. (4) indicates that a second component, if present in an appreciable amount ($R_{21} \approx 1$), either has a lifetime less than 1.3 msec or greater than 0.7 msec. Furthermore, a straight line least-squares fitted to the first half of an experimental decay plot, such as Fig. 4, has the same slope to within the accuracy of the fit as a straight line fitted to the second half. Therefore all runs—50 for ortho-H_2, 8 for para-H_2, 24 for D_2, and 20 for HD—are fitted according to Eq. (4) with a least-squares straight line to obtain a single lifetime τ from the slope ($=-1/\tau$). As in Fig. 4, the fit is only to data points corresponding to a number of counts greater than 10% of the peak value.

The result for the lifetime of the $c\,^3\Pi_u$ metastable state is $\tau = 1.02 \pm 0.05$ msec, and is the same for both para- and ortho-H_2, as well as for D_2 and HD. Since all three isotopic combinations have the same measured lifetime, and since the lifetime for a forbidden predissociation through spin-orbit mixing with the $^3\Sigma_u^+$ state would be expected to depend upon details of the fine structure, we conclude that our value of $\tau = 1.02 \pm 0.05$ msec is the radiative lifetime for a combination of magnetic-dipole electric-quadrupole decay of the $v=0$ $^3\Pi_u$ state to the repulsive $^3\Sigma_u^+$ state. The failure to observe any difference in the lifetime also lends additional support to our conclusion that the metastable states in the beam all decay at a single uniform rate, and implies that forbidden predissociation decay, if predominant for any $^3\Pi_u$ level, results in a lifetime somewhat shorter than 0.4 msec, the minimum time of flight in our apparatus.

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