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DIRECT MEASUREMENTS OF PREDISSOCIATION PROBABILITIES IN CH AND CD MOLECULES*

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Quantitative measurements of nonradiative decay rates in the $C^2\Sigma^+$ state of CH and CD molecules are presented via absolute phase shift versus frequency data and are interpreted as direct measures of predissociation probabilities. The C-state decay rates measured in CH are approximately three times larger than those in CD and comparison with absorption oscillator strength measurements shows that the predissociation probabilities of the rotational levels observed in CH range from approximately 3×10^7 to 1.6×10^8 sec^{-1}, i.e., approximately 3 to 18 times the radiative transition probability.

The visible and near ultraviolet emission spectra of CH and CD have been known for some time,[1] and the transitions in CH have been identified in solar, stellar, and interstellar absorption.[2] Einstein transition rates, A, have recently been measured for two of the three known emission systems in CH, viz., for $A^2\Delta - X^2\Pi$ and $B^2\Sigma^- - X^2\Pi$.[3,4] Herbig[5] has deduced an approximate absorption oscillator strength for the $C^2\Sigma^+ - X^2\Pi$ transition at 3144 Å relative to the A-X and B-X transitions from the observed equivalent widths of the interstellar CH lines in the spectrum of ζ Ophiuchi. Linevsky[6] has recently reported the first laboratory measurement of a relative f value for the C-X system, using a King furnace; his value of $f(C\text{-}X)/f(A\text{-}X) = 1.26$, if put on an absolute scale using Fink and Welge's[4] A-X transition probability, leads to a radiative lifetime of 115 nsec for the C state. The corresponding value derived from Herbig's estimate would be 430 nsec.[7]

In recent flash-photolysis experiments with CH_2N_2 and CD_2N_2 Herzberg[8] noted that although C-X fluorescence is observed in the spectrum of the deuterated compound, it is absent or weaker by a factor of at least 5 in the normal compound. He has interpreted this intensity difference between the two isotopes as evidence for a weak predissociation affecting the C state

of CH even though the C-X transition of CH is regularly seen in emission in discharges and flames, where it is, however, much weaker than the A-X and B-X emissions in both CH and CD. No anomalies have been reported in the rotational intensity distribution of the C-X emission.[1,9]

We have measured the decay rate of the $C^2\Sigma^+$, $v' = 0$ level in CH and in CD at low pressures using the phase shift apparatus of Lawrence[10,11] in which emission spectra are excited by an rf-modulated beam of low-energy electrons. We have found a substantially more rapid decay than is consistent with the lifetime for purely radiative decay expected from the absorption measurements of either Linevsky or Herbig.

CH_4 of high chemical purity and CD_4 of high isotopic purity[12] were used for electron-beam excitation of the C-X emission of CH and CD and the phase shifts were determined using the Ne-II multiplet at 1908-1935 Å as an absolute phase reference.[11] Electron energies of 100 V were used for these measurements, after careful investigation had shown no dependence of the phase shifts on electron energy in the range from 90 to 200 V and no dependence on pressure in the excitation region over a workable range from about 1 to 11 μ. With equal pressures of the parent molecules in the

excitation region, the emission intensity of
CH $C-X$, excited in CH_4, is three to four times
weaker than the corresponding CD C-X emis-
sion, excited in CD_4. The phase versus frequen-
cy curves of the C-X transitions in CH and CD
are shown in Fig. 1 along with theoretical phase
versus frequency curves computed from $\tan\varphi$
$= 2\pi f\tau$ (f = modulation frequency, τ = radiative
lifetime), for pure exponential decays with life-
times of 6.5 and 55 nsec. Apart from some
distortion of the measured phase curves due
to the presence of a range of decay rates (see
below), it is immediately evident that: (1) The
lifetimes present in CH and CD differ marked-
ly from each other, with CH showing the short-
er lifetimes; and (2) that all lifetimes through-
out the range covered by either isotope are
markedly shorter than the radiative lifetime
corresponding to Linevsky's f value. These
results immediately confirm Herzberg's inter-
pretation of the comparative weakness of the
CH emission as evidence for weak predissoci-
ation of the C state. They further show that
an even weaker predissociation affects the C
state of CD.

The observed phase curves in CH and CD
(Fig. 1) cannot be represented by pure exponen-
tial decays with a unique lifetime for each iso-
tope. The curves could in principle be inter-
preted in terms of unique C-state lifetimes com-
bined with radiative cascading from longer lived,
higher lying, excited states. However, no high-
er lying states have ever been observed in emis-
sion despite careful searches. The observa-
tions can be plausibly assigned to spectrally
unresolved overlapping of emissions from C-
state rotational levels covering a range of pre-
dissociation probabilities. A numerical anal-
ysis of the phase data of Fig. 1 was carried
out based on the simplifying assumption of over-
lapping of emission from states of only two
distinct lifetimes. Good fits to the CH and CD
phase shifts at all frequencies were obtained
on that basis with lifetimes of 6 and 26 nsec
in CH and of 18 and 55 nsec in CD. These val-
ues indicate the approximate ranges over which
the lifetimes of the individual rotational levels
of CH and CD must vary to produce the observed
phase curves. The levels for which these find-
ings apply are those contributing to an 8-Å wide
region around the peak of the C-X (0, 0) emis-
sion band, corresponding to the band selected
by the monochromator for the phase measure-
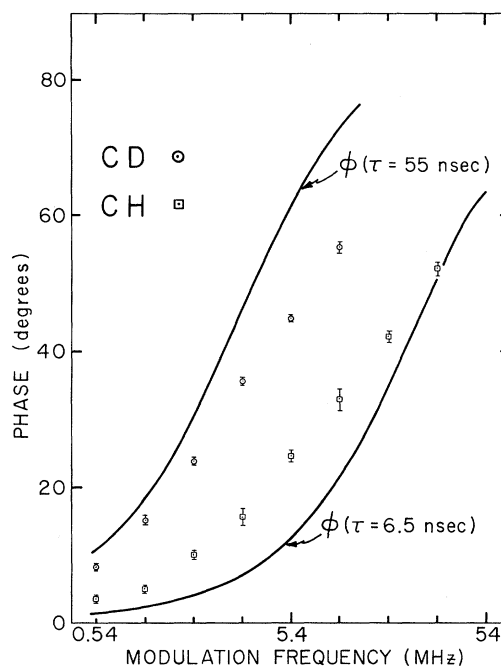ments. The probabilities for predissociation

FIG. 1. Phase shift versus frequency data obtained
for the $C\,^2\Sigma^+$ states of CH and CD. By comparison with
the solid curves corresponding to exponential decays
of 6.5 and 55 nsec, one may readily see the two effects
reported in this work, namely the short mean lives of
the $^2\Sigma^+$ states in both CH and CD and the change in
mean life in CD compared with CH.

corresponding to the observed spread of life-
times are 3×10^7 to 1.6×10^8 sec^{-1} in CH and
9×10^6 to 4.7×10^7 sec^{-1} in CD, after subtract-
ing the radiative contribution of 9×10^6 sec^{-1}
as determined from Linevsky's[6] and Fink and
Welge's[4] measurements. This is probably the
weakest predissociation that has been recog-
nized and positively identified in a case where
an entire emission band is observed at low pres-
sure over the complete range of expected J
values without any obvious anomalies in the
rotational intensity distribution. The results
reported above also constitute the first direct,
quantitative measurements of probabilities for
predissociation through determination of decay
constants.

The only dissociation limit lying below the
$v' = 0$ level of the $C^2\Sigma^+$ state is the limit corre-
sponding to atomic C and H in their normal states,
$^3P + ^2S$. None of the molecular states correlat-
ing with that limit: $X^2\Pi$, $B\,^2\Sigma^-$, and the two
predicted states $^4\Sigma^-$ and $^4\Pi$, would lead to an
allowed predissociation of the $C^2\Sigma^+$ state (the
ground state, $X^2\Pi$, can be excluded because

of the Franck-Condon principle). The variation of predissociation with rotation could be caused either by a modification of a rotation-dependent, approximate selection rule (e.g., a change of coupling case in the $^4\Pi$ state with increasing rotation of the molecule), or by a variation of a tunneling probability due to the dependence of effective potential curves on rotational energy. Attempts will be made to determine whether the predissociation probability increases or decreases with J value in order to eliminate some of these possibilities.

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