Frequency shift of hyperfine transition $\Delta m_F = 0$ of the ground state of an H atom chemically interacting with molecules in the gas phase

E. B. Gordon, B. I. Ivanov, A. P. Perminov, V. E. Balalaev, F. F. Datchenko, and A. N. Ponomarev

Institute of Chemical Physics, USSR Academy of Sciences

We have observed experimentally large frequency shifts of the hyperfine transition ($\lambda = 21$ cm) of the H atom, due to its chemical interaction with CO and SO_2 molecules in the gas phase. The effect is attributed to the abrupt decrease of the hyperfine splitting in the short-lived intermediate complex.

PACS numbers: 35.20.S, 34.50.L

The interaction of an atom emitting at a frequency ω_0 with atoms and molecules in the gas phase leads to a Lorentz line shape of the transition with a broadening $\Delta\omega$ and a frequency shift $\delta\omega$ determined by the average phase shift $\bar{\Phi}$ per collision (see the reviews[1,2]). According to theoretical and experimental investigations, the frequency shift of the hyperfine (*hf*) transition $(F = 1, m_F = 0) \rightarrow (F = 0, m_F = 0)$ of the ground state of the hydrogen atoms is due to the following mechanisms: a) Van der Waals attraction ($\Phi < 0$) and Pauli repulsion ($\Phi > 0$), which partially cancel each other; in this case $|\bar{\Phi}| \approx 10^{-4}$ rad/collision, and $\delta\omega \gg \Delta\omega$; b) spin exchange with electrons and paramagnetic molecules (when the latter are previously polarized by electron spin, then $|\bar{\Phi}| \approx 10^2$ rad/collision and $\delta\omega/\Delta\omega \sim 10^{-1}$–$10^{-2}$; in the absence of polarization we have $\bar{\Phi} = 0$). In accord with the foregoing, the experimentally observed shifts of the hyperfine transition of the H atoms with the inert-gas atoms and diamagnetic molecules do not exceed 30 Hz/Torr.

Investigations of elementary chemical processes of H atoms with the aid of a hydrogen laser[3,4] have raised the question of experimentally observing much larger frequency shifts of the *hf* transition, due to the interaction of the H atoms with molecules *M* capable of entering in chemical reaction with the hydrogen. Such shifts can take place if the decay of the intermediate complex H*M* (if this complex is not stabilized by collisions) proceeds via the reverse channel, i.e., into the initial particles H and *M*. The chemical interaction decreases the density of the unpaired electrons at the protons, and according to[5] decreases the splitting in the complex.

From the EPR spectra of hydrocarbons it follows that the frequencies of the *hf* transitions of their hydrogen atoms are at least 20 times smaller than in the free H atom.[6] It can therefore be assumed that the hyperfine interaction is "turned off" during the lifetime τ_c of the complex, and $\Phi_{chem} = -\omega_0\tau_c$.

We have measured the shifts of the center of the emission line of a hydrogen laser operating far from self-excitation in the regime of amplification of a constant microwave signal, following admission of different molecular gases into its storage flask. The obtained frequency shifts $\delta\omega$ and the values of the ratio $\delta\omega/\Delta\omega$ estimated from the corresponding line broadening $\Delta\omega$ are listed in the table. The accuracy with which the shifts were measured, which determined the frequency instability of the reference generator (a rubidium frequency meter Ch1−43) and the signal/noise ratio, amounted to $(\omega - \omega_0)/\omega_0 \approx (3-5) \times 10^{-11}$. To eliminate the frequency drift due to the temperature-induced detuning of the microwave resonator, the resonator temperature was stabilized with accuracy $\pm 0.02°$ near 32 °C.

As seen from the table, the polarizabilities of the investigated molecules, which determine the magnitude of the Van der Waals interaction, are close to one another; this means that the corresponding collision frequency shifts of the hyperfine transition of the H atom should be approximately equal.

Indeed, our experiment did not reveal any frequency shift following collisions of H atoms with N_2O molecules, in which the probability of the formation of the complex HN_2O is small ($< 10^{-5}$ per collision). Nor were frequency

M	n_H, cm^{-3}	n_M, cm^{-3}	$\alpha \cdot 10^{25}$, cm^3	$\delta\omega$, Hz/Torr	$\lvert \delta\omega/\Delta\omega \rvert$
CO	$1 \cdot 10^8$	$(4 \div 10) \cdot 10^{13}$	19.5	-71 ± 25	$\geqslant 0.2^{1)}$
SO_2	$1 \cdot 10^8$	$(1 \div 5) \cdot 10^{13}$	37.5	-415 ± 60	0.25
N_2O	$1 \cdot 10^8$	$2.6 \cdot 10^{14}$	30.0	$\leqslant 3$	–
O_2	$1 \cdot 10^8$	$5.0 \cdot 10^{10}$	16.0	$\leqslant 2 \cdot 10^4$	$\leqslant 0.012$

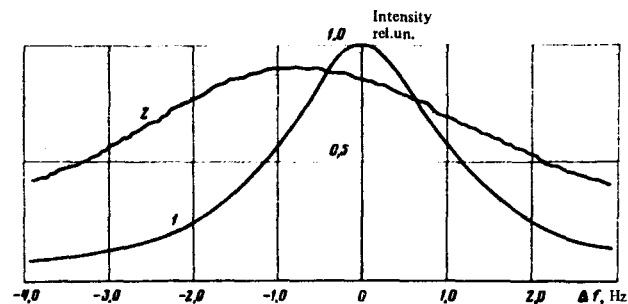n_H and n_M are the concentrations of the H atoms and of the molecules, respectively.

1) It is possible that the broadening in this case is due to an oxygen impurity amounting 10^{-3} rel.%.

Frequency shift of the emission of H atoms following admission of SO_2 molecules into the hydrogen-laser storage flask; the scale of line 2 is larger by one order of magnitude.

...ions observed against the background of the spin-exchange broadening in the case of interaction of the H atoms with paramagnetic O_2 molecules. This result confirms the theoretical calculations, according to which $\delta\omega = 0$ in spin exchange with unpolarized molecules. [8] 1)

The H atoms can combine, with noticeable probability, as they collide with the diamagnetic CO and SO_2 molecules. [9] The result is a free radical HM, which is excited above the dissociation energy, and which decays (in the absence of stabilization) into the initial particles. The observation of the frequency shift due to the short-duration chemical binding is also favored by the fact that in view of the small number of atoms, the lifetime of the complex is $\tau_c \lesssim \omega_0^{-1}$. The figure demonstrates the shift and broadening of the line of the *hf* transition ($\Delta m_F = 0$) of the H atoms as they collide with SO_2 molecules. The frequency shifts observed for CO in SO_2 (see the table) greatly exceed the largest of the known collision frequency shifts on the atoms Xe, which are extremely easy to polarize ($\alpha = 37 \times 10^{-25}$ cm^3), where $\delta\omega = 30$ Hz/Torr. [10]

It follows from the results that a purposeful study of the frequency shifts of the *hf* transition of the H atom as it interacts chemically with different molecules can yield information on the probability of production of an intermediate complex, on its lifetime, and on the temperature dependences of these quantities.

1)These measurements are at the same time convincing proof that the change of the Q of the line (its broadening) does not effect the measured frequency of the HF transitions.

[1]I. I. Sobel'man, Vvedenie v teoriyu atomnykh spektrov (Introduction to the Theory of Atomic Spectra), Moscow (1963).
[2]W. Happer, Rev. Mod. Phys. **44**, 169 (1972).
[3]E. B. Gordon, A. P. Perminov, B. I. Ivanov, V. I. Matyushenko, A. N. Ponomarev, and V. L. Tal'roze, Zh. Eksp. Teor. Fiz. **63**, 401 (1972) [Sov. Phys.-JETP **36**, 212 (1973)].
[4]E. B. Gordon, B. I. Ivanov, A. P. Perminov, A. N. Ponomarev, V. L. Tal'roze, and S. G. Khidirov, ZhETF Pis. Red. **17**, 548 (1973) [JETP Lett. **17**, 395 (1973)].
[5]E. Fermi, Zs. Phys. **60**, 320 (1930).
[6]A. Carrington and A. D. McLachlan, Magnetic Resonance with Applications to Chemistry, Harper & Row, 1967.
[7]Landolt-Börnstein, "Zahlenwerte und Funktionen", B. 3, S 510 (1950).
[8]L. C. Balling, R. J. Hanson, and F. M. Pipkin, Phys. Rev. **133**, A607 (1964).
[9]V. N. Kondrat'ev, Konstanty skoroski gazofaznykh reaktsii (Rate Constants of Gas-Phase Reactions), Nauka (1970).
[10]E. S. Ensberg and C. L. Morgan, Phys. Lett. **28**, 106 (1968).