On Acoustic Dispersion In MF$_6$-type Molecules

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Abstract

Available data on relaxation times in MF$_6$-type molecule have been incompatible with analytical approaches. Then, we performed experiments on the acoustic dispersion of SF$_6$, WF$_6$ and UF$_6$ gases by using a double crystal ultrasonic interferometer. It was revealed that the available data on WF$_6$ are not acceptable, and the relaxation time of UF$_6$ is less than 0.027 μsec·atm at a temperature below 68°C.

1. Introduction

Experimental data on relaxation times in MF$_6$-type molecules are available for SF$_6$[1-8] and WF$_6$.[8] Comparing those data with each other, the relaxation time for SF$_6$, τ_s, is at most a few times larger than that for WF$_6$, τ_w, at room temperature. On the other hand, an analytical consideration leads to the expectation[9] that τ_s would be larger than τ_w by a factor of $\sim 10^2$. The discrepancy between the experimental data and the analytical expectation seems too large to be corrected by further analytical approaches.

By using a double crystal ultrasonic interferometer,[10] we measured the sound velocity of SF$_6$, WF$_6$, and UF$_6$ in the range of frequency/pressure ratio, f/P, up to 10 MHz/atm.

The obtained relaxation times for SF$_6$ agreed fairly well with the available data. However, as for WF$_6$, our results were quite different from the previous measurements.[8] It may be considered that the discrepancy between experimental data and analytical expectations was caused by the previous measurements on WF$_6$.

If the relaxation times of UF$_6$, τ_u, were large enough ,one should take this matter into account as regards the design of compressors used in uranium enrichment plants by

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the gaseous diffusion process and the ultracentrifuge process. According to the results obtained, however, τ_u is so small that the vibrational relaxation phenomenon in UF_6 never affects it.

2. Experimental

Fig. 1 shows the double crystal ultrasonic interferometer used to measure the sound velocity in SF_6, WF_6 and UF_6. The measuring chamber is a cylindrical stainless-steel tube of 7.6 cm in diameter. Two crystals of gold-plated lead titanate (4 cm in diameter) are placed in the chamber opposite each other. Since the upper crystal is connected to the micrometer, the distance between the crystals is variable by 4 to 45 mm. The moving distance can be determined to an accuracy of $\sim 2\,\mu m$.

Three pairs of crystals of 46.4 KHz, 329.9 KHz and 2.384 MHz were prepared to equip alternatively in accordance with the required range of f/P. However, the pair of crystals of 2.384 MHz was impractical because of a large classical ultrasonic absorption of hexafluoride gases at low pressure. Ring gaskets 2 mm in thickness were interposed as shown in Fig. 1 to prevent the transmission of mechanical noises through the solid walls of the chamber. The temperature in the interferometer placed in an air bath changed from room temperature to 90°C. The pressure was measured by a Helicoid
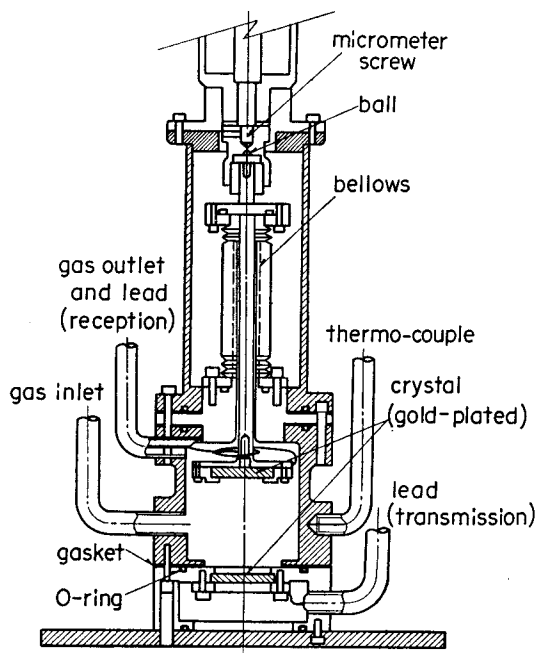

Fig. 1. Double crystal ultrasonic interferometer.

gauge from 0 to 2 atm. The variable range of f/P was in practice from 0.025 to 10 MHz/atm.

The gases were introduced into, and withdrawn from, the interferometer through nickel pipes and Monel valves. The experimental system was subjected to baking and passivation with fluorine to prevent WF_6 and UF_6 from decomposition. The leak rate of air was less than $10 \, \mu Hg/hr$.

SF_6, with a 99.8% specified minimum purity from Matheson Inc., was used after freeze-thaw outgassing cycles. Hydrogen fluoride of $\sim 0.4\%$ in purchased WF_6 was detected by an infrared spectrometer with a window of CaF_2. WF_6 introduced into the interferometer after bulb-to-bulb distillations. UF_6 prepared from the reaction between UO_2 and F_2 was also subjected to bulb-to-bulb distillations just before usage.

For the dtermination of sound velocity, the intensity of the electrical signal induced on the receiving crystal was measured on changing the distance between the crystals, and the shape of the signal was monitored by an oscilloscope.

To confirm the sufficient accuracy of the sound velocity obtained by the interferometer, sound velocities in He, N_2 and Ar were measured. The results coincided with available data.[12]

3. Results and Discussion

For precise measurements of sound velocity, corrections for the deviation of the gas from the behavior of ideal gases must be considered even in the neighborhood of 1 atm. The first order correction by which to multiply the experimental velocity, v, to arrive at the idealized velocity, v_i, can be expressed as follows:

$$(v/v_i) = 1 - gP \tag{1}$$

wich corresponds to v at an extremely low pressure. g can be calculated from the second virial coefficient or Lennard-Jones potential parameters.[13] If P is in atomosphere, g lies in the order of 10^{-2} for SF_6, WF_6 and UF_6 at 1 atm.

In the region of ultrasonic dispersion, sound velocity varies also with $q \equiv f/P$. In the case of a single dispersion, the dependence of v_i on q can be written as follows:

$$\frac{v_i^2}{v_0^2} = 1 + \sum_{j=1}^{6} \frac{D_j \omega^2 \tau_j}{1 + \omega^2 \tau_j^2} \cong 1 + \left\{ \left(\frac{v_\infty}{v_0}\right)^2 - 1 \right\} \frac{(q/q_h)^2}{1 + (q/q_h)^2}. \tag{2}$$

ω denotes the angular frequency. τ_j's and D_j's are effective acoustic relaxation times as well as associated relaxation constants. Those are closely related to six different vibrational modes of MF_6-type molecules. v_0 and v_∞ represent low- and high frequency idealized velocities, respectively. q_h is q at the half-point between v_0^2 and v_∞^2.

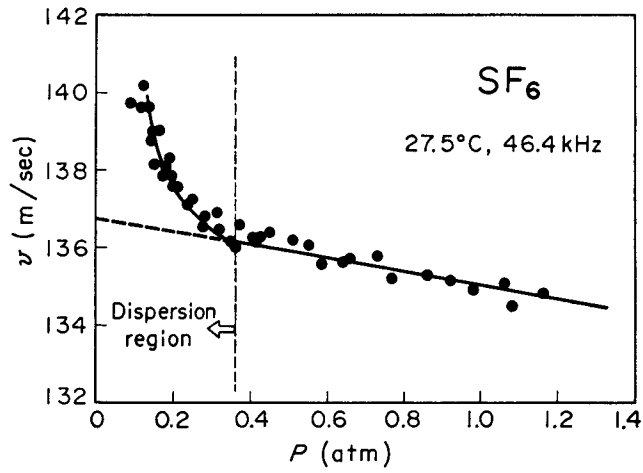Fig. 2 shows the result obtained by using crystals of 46.4 KHz, in which one may

Fig. 2.   Affect of nonideality and ultrasonic dispersion on the sound velocity in SF$_6$.

Table 1.   Values of parameter g.

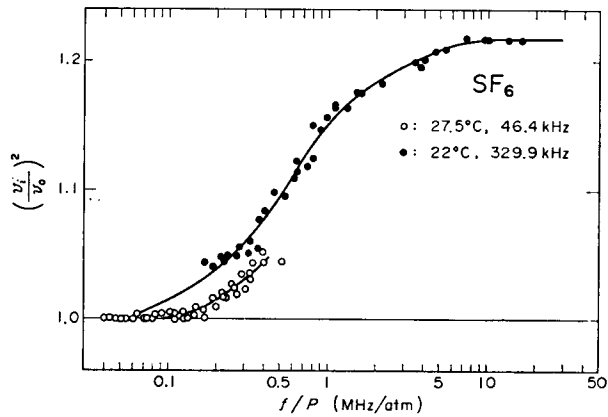|	SF$_6$	WF$_6$	UF$_6$
T(°C)	25.2	22.0	77.0
f(KHz)	46.4	329.9	329.9
$g_{obs.}$(1/atm)	0.015	0.029	0.025
$g_{calc.}$(1/atm)	0.009	0.024	0.021
L-J parameters	Ref. 15	Ref. 16	Ref. 17

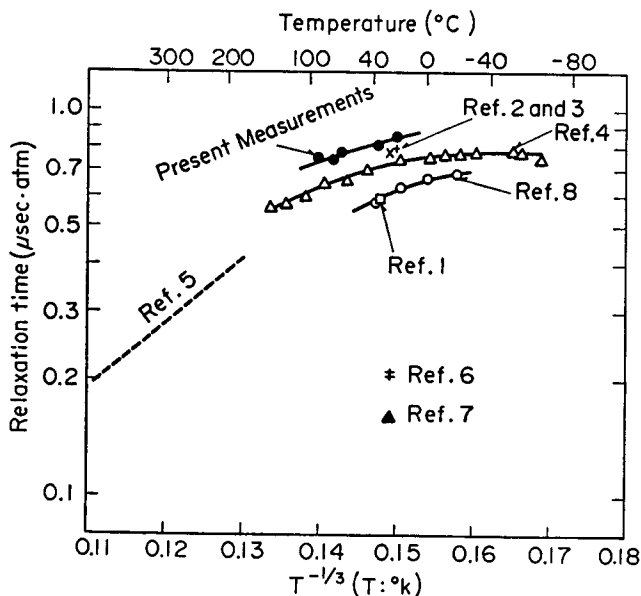Fig. 3.   Examples of observed dispersion curve of SF$_6$.

Fig. 4. Comparison of data on vibrational relaxation time of SF₆.

find the effects of non-ideality and dispersion on sound velocity. In the region over 0.35 atm ($f/P>$0.133 MHz/atm), the plots lay on an almost straight line. The gradient and the intercept on the coordinate axis of the sextrapolated line correspond to g and v_0, respectively. The values of g for SF₆, WF₆ and UF₆ are tabulated in Table 1.

Ultrasonic dispersions of SF₆ were observed under the conditions of q up to 10 MHz/atm and $19<T<87°C$, an example of which is presented in Fig. 3. Correction of non-ideality was made by using g calculated from Lennard-Jones potential parameters.

Adjusted relaxation times[2,6], $P·\tau_s$(μsec·atm), were calculated from the half-point of each velocity-dispersion curve and ultrasonic absoprtion curve. They are shown in Fig. 4 as a function of temperature together with previous measurements. As can be seen, our results almost agree with the previous bulk-thermal (ultrasonic and shock-wave densitometric) measurements.

As shown by the broken line in Fig. 5, Hodkinson and North[8] have reported a velocity dispersion in WF₆ appearing in an unusually narrow region from 1 to 3 MHz/atm. They obtained the relaxation time for WF₆ from their measurements of ultrasonic absorption and dispersion at a temperature from 10 to 41°C. According to their results, $P·\tau_w$ is around 0.27 μsec within the above temperature range.

The present results for WF₆ are shown in Fig. 5. We did not find any velocity dispersion nor any characteristic change of the attenuation coefficient for WF₆ in the region from 0.3 to 10 MHz/atm. We have to conclude that the available data for WF₆ are not
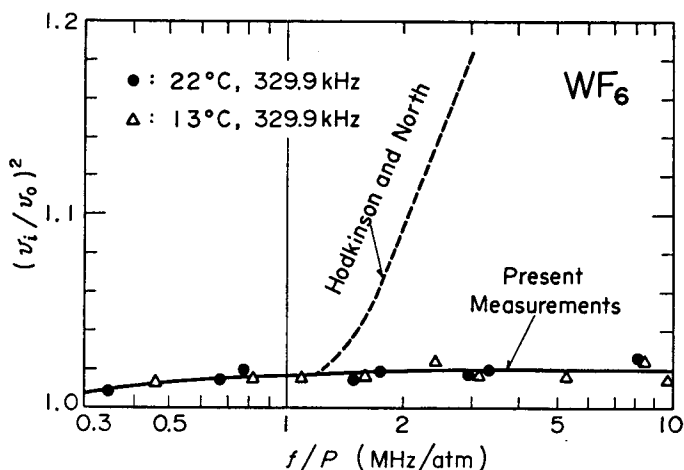
Fig. 5.   Observed sound velocity in WF_6 and previous measurements.

acceptable.

As in WF_6, we could not find any velocity dispersion in UF_6 in the region below 10 MHz/atm at 68 to 76.5°C.

Because f/P should vary by a factor $\sim$10 to cover the whole dispersion curve, one may consider that the half-points for WF_6 and UF_6 would appear at the region of f/P higher than at least 30 MHz/atm.   It follows that $P \cdot \tau_w$ and $P \cdot \tau_u$ should be less than 0.023 μsec·atm (>13°C) and 0.027 μsec·atm (>68°C), respectively.   Even these ceiling values of $P \cdot \tau_w$ and $P \cdot \tau_u$ are much smaller than $P \cdot \tau_s$ presented in Fig. 4.   Such an experimental result is compatiable with the analytical expectation.[9]   The determination of relaxation times in WF_6 and UF_6 is the subject for a future study.

Acknowledgements

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