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The Pressure Broadening of HDO by O_2, N_2, H_2, and He between 100 K and 600 K

by

Thomas M. Goyette, David W. Ferguson, and Frank C. De Lucia
Department of Physics
Ohio State University
Columbus, OH 43210

and

J. M. Dutta and C. R. Jones
Department of Physics
North Carolina Central University
Durham, NC 27707

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ABSTRACT

Microwave transitions of HDO pressure-broadened by H_2, O_2, N_2, and He were studied in the temperature region between 100 K and 600 K. Measurements below 250 K were made in a collisionally cooled cell. Above this temperature a conventional equilibrium cell was used in the region where the HDO has non-negligible vapor pressure. Significant variations in both the pressure broadening parameter and its temperature dependence were observed among the studied transitions. Ordinarily, a power law is used to describe this temperature dependence. Deviations from this were observed below 150 K.

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I. INTRODUCTION

The purpose of this paper is to provide experimental measurements of pressure broadening over a wide range of temperatures. This provides tests for theoretical methods designed to calculate these parameters from a more fundamental set of molecular constants such as dipole and quadrupole moments[1,2]. HDO and the collision partners H_2, O_2, N_2, and He were chosen as the subject of this work to compliment earlier work on HNO_3, H_2O, and NO_2 [3-8]in order to provide the best possible mix of data for this purpose. Applications in both astronomy and atmospheric science also led to this choice of collision partners. The wide range of temperatures studied in this work is particularly important both to provide for a more stringent theoretical test and because of the many applications at non-ambient temperatures. Perhaps the most interesting result of this study is the observation of significant deviations at low temperature from the power law ordinarily used to describe the change of pressure broadening parameter with temperature.

II. EXPERIMENTAL

We have previously discussed the general millimeter wave and pressure broadening techniques used in this work and will be brief here[3,9,10]. The measurements at temperatures for which water has a vanishingly small vapor pressure were made in the collisionally cooled cell shown in Fig. 1. In practice its temperature is continuously variable from 80 to 300K, with the usable upper limit set by the trapping point of the spectroscopic gas. The cell is a 4-inch diameter copper pipe, 1 foot in length, with 2-inch diameter end sections with Brewster's angle flanges. Indium sealed 0.005-inch Mylar windows are attached to the flanges. In order to provide a uniform temperature, the cell is surrounded by a copper jacket 5 feet in length with cooling coils attached, and a 7-foot fiberglass jacket. The spectroscopic sample flows into the cell through the injector seen in the middle of the figure, where the injector temperature is kept above the freezing point of the sample. The cell is filled with a background pressure of broadening gas, and the sample molecules cool by collisions with the cold background gas, eventually random walking their way to the walls where they condense. Higher temperature observations are made in a conventional equilibrium cell which can either be cooled by flowing nitrogen gas or heated electrically. The millimeter radiation is generated by harmonic generation, propagated quasi-optically through the cell, and detected by an InSb detector operating at 1.6 K.

Measurements are made in the collisionally cooled cell by establishing a flow of the spectroscopic gas into the cell from the injector and incrementally adding the collision partner to the cell via a computer controlled valve. The data acquisition computer then automatically records the lineshape for each of about 40 pressures in the range between ~0.01 and 1.0 Torr. Pressure broadening parameters are recovered from these data by first fitting them to a Voigt profile to obtain the pressure broadening contribution to the lineshape. These contributions are then fit to the linear function which relates linewidth, pressure, and pressure broadening parameter. A typical result is shown in Fig. 2. A similar procedure is used in the equilibrium cell, except that initially a small amount (typically 10 mTorr), of HDO is placed in the cell before the

broadening gas is incrementally added.

III. RESULTS

Figures 3 - 5 show the results of the pressure broadening studies on the $2_{1,1}$ - $2_{1,2}$, $3_{1,2}$ - $2_{2,1}$, and $7_{3,4}$ - $6_{4,3}$ transitions of HDO broadened by He, O_2, N_2 and H_2. These results are also shown numerically in Table I. The variation of pressure broadening parameter with temperature is often described by

$$\gamma(T)=\gamma_0(T_0/T)^n \qquad (1)$$

where γ_0 is the broadening parameter at reference temperature T_0 (300 K for this work) and n is a constant. Since this relation has been found to be generally valid near ambient temperatures where most pressure broadening measurements have been made, it has been used to great advantage to simplify the parametrization of data bases[11].

In order to compare the results of our work with this relation, the data of Figs. 3 - 5 have been replotted logarithmically in Figs. 6 - 8 and compared with the straight line given by Eq. 1 in the logarithmic representation. In these figures the graphs of Eq. 1 for each case were determined by fitting the higher temperature points for which this relation is valid. The numerical results are shown in Table II. It can be seen in the figures that all helium data points for the three transitions can be fit by this equation. Furthermore, n is found to equal 0.5, the result expected from the simplest hard sphere theory. However, for oxygen, nitrogen and hydrogen only the higher temperature points can be fit since the data at the lowest temperatures begin to fall below the value predicted by the higher temperature data set.

IV. DISCUSSION

The number of observations of pressure broadening for polyatomic molecules over a relatively large range of temperature is small. Observations have now been made over the region from ~ 100 - 600 K for HNO_3, H_2O, and HDO in collision with H_2, He, O_2, and N_2[4,5,6]. The broader temperature range covered by this work leads to both more accurate values of n and to observation of deviation from Eq. 1. Thus, they provide a particularly interesting set of experimental results against which theories can be developed and tested.

For this work on HDO there is a large variation of room temperature pressure broadening parameter γ_0 with quantum number, which can be easily seen both in the graphs and in Table II. For all broadening gases the pressure broadening parameter decreases with increasing J and energy, the largest change occurring in oxygen broadening where there is a decrease of 42%. The n values for helium show no significant change with quantum number from the classically predicted $n = 0.5$, a result that indicates the collision cross sections are remaining constant. However, there is significant variation in the value of n for collisions involving oxygen, nitrogen and hydrogen. The largest change occurs in the hydrogen broadening, for which the value of n changes by 31%. This result is easily seen in the plot of hydrogen broadening where the data set for the $7_{3,4} - 6_{4,3}$ has a significantly different slope from the other transitions.

Perhaps the most interesting of the results obtained in this work are those obtained at temperatures below ~150 K where deviations from Eq. 1 occur for all collision partners except He. All semi-classical Anderson like theories predict that there exists a temperature, below which the Fourier components of the collision are no longer effective for the creation of broadening. These are manifest in the parameter $k = (b/\omega)/v$ which effectively compares the Fourier frequencies produced by the molecule passing with velocity v within collision parameter b and the rotational transition frequency ω[12]. In this context it is no surprise that helium is the most hard sphere like. It has no internal degrees of freedom to come into resonance with the Fourier components of the collision and the energy levels of HDO connected to the observed transitions are, although

relatively widely spaced, closely spaced in comparison to the spectrum of the collision. Although H_2 is even lighter than He and thus in collisions produces even a broader spectrum, it has very widely spaced rotational energy levels of its own which can participate in the energetics of the collision. In fact, we find in our previous studies the decrease in observed cross section below that given by Eq. 1 to be a general feature of H_2 broadening . For example, Figs. 9 and 10 show the H_2 pressure broadening parameters of the $3_{1,3} - 2_{2,0}$ and $4_{1,4} - 3_{2,1}$ transitions of H_2O, respectively. Comparison with the He results leads to a strong indication that this effect is due to the internal energy levels of H_2[6.7]. The O_2 and N_2 results show a similar short fall. Again this result is consistent with our observations on other species[3,5]. However, in these cases both O_2 and N_2 are much heavier than either H_2 or He and the appropriate comparison should be between the much lower frequency spectrum produced in their collisions and the energy level spacings of HDO and O_2 and N_2 themselves.

Finally, it should be noted that in other work which has extended these measurements to very low temperatures (~4 K) significant new phenomena associated with quasibound states are observed for collisions with both H_2 and He[13]. Specifically, these quasibound states lead to the formation of large resonances in the pressure broadening cross sections at low temperature. Thus, although the semiclassical theory considered here leads unambiguously to a lowering of cross section at very low temperature, these new processes often lead to significantly increased cross sections at low temperature.

V. ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1. Collisionally cooled cell for the measurement of pressure broadening at low temperature.

Figure 2. Measured half-widths as a function of pressure for the $3_{1,2} - 2_{2,1}$ transition of HDO broadened by H_2.

Figure 3. Pressure broadening parameter for the $2_{1,1} - 2_{1,2}$ transition of HDO as a function of temperature for broadening by He(solid square), H_2(solid circle), O_2(open circle), and N_2(open square).

Figure 4. Pressure broadening parameter for the $3_{1,2} - 2_{2,1}$ transition of HDO as a function of temperature for broadening by He(solid square), H_2(solid circle), O_2(open circle), and N_2(open square).

Figure 5. Pressure broadening parameter for the $7_{3,4} - 6_{4,3}$ transition of HDO as a function of temperature for broadening by He(solid square), H_2(solid circle), O_2(open circle), and N_2(open square).

Figure 6. Log plot of the pressure broadening parameter for the $2_{1,1} - 2_{1,2}$ transition of HDO as a function of temperature for broadening by He(solid square), H_2(solid circle), O_2(open circle), and N_2(open square).

Figure 7. Log plot of the pressure broadening parameter for the $3_{1,2} - 2_{2,1}$ transition of HDO as a function of temperature for broadening by He(solid square), H_2(solid circle), O_2(open circle), and N_2(open square).

Figure 8. Log plot of the pressure broadening parameter for the $7_{3,4} - 6_{4,3}$ transition of HDO as a function of temperature for broadening by He(solid square), H_2(solid circle), O_2(open circle), and N_2(open square).

Figure 9. The H_2 pressure broadening parameters of the $3_{1,3} - 2_{2,0}$ transition of H_2O.

Figure 10. The H_2 pressure broadening parameters of the $4_{1,4} - 3_{2,1}$ transition of H_2O.

TABLE I

The He, H_2, O_2, and N_2 Broadening Parameters of HDO.[a]

T(K)	γ(MHz/Torr)			
	He	H_2	O_2	N_2
	$2_{1,1}$-$2_{1,2}$ 241561.55 MHz			
121	1.06	6.25	4.60	6.70
127	1.28	7.01	4.51	6.27
139	1.15	6.12	4.37	6.59
139	1.11	5.84	4.27	6.58
149	1.14	6.02		6.71
150	1.27		4.37	6.18
151	1.18	5.96	4.49	6.61
160	1.16	5.75	4.44	6.80
171	1.04	5.31	4.49	6.63
241	0.86	4.58	3.29	5.21
298	0.80	3.97	2.67	4.51
357	0.71	3.35	2.31	3.89
419	0.66	2.87	2.01	3.41
508	0.59	2.39	1.58	2.95
	$3_{1,2}$-$2_{2,1}$ 225896.70 MHz			
90	1.07	5.81	4.25	6.19
105	1.37	5.68	3.94	6.24
113	1.17	5.68	4.25	6.77
124	1.12	5.58	4.10	6.67
142	1.09	5.62	4.22	6.85
147	1.00	5.51	4.03	6.61
159	0.99	5.32	4.04	6.61
175	1.03	5.20	3.88	6.14
241	0.79	4.12	2.81	4.88
298	0.74	3.59	2.33	4.26
388	0.63	2.74	1.71	3.45
450	0.59	2.40	1.50	3.10
518	0.55	2.20	1.35	2.90
	$7_{3,4}$-$6_{4,3}$ 241973.50 MHz			
241	0.57	2.86	1.90	3.99
298	0.52	2.44	1.54	3.49
394	0.45	2.15	1.29	2.79
457	0.42	1.97	1.11	2.63
561	0.37	1.68	0.96	2.27

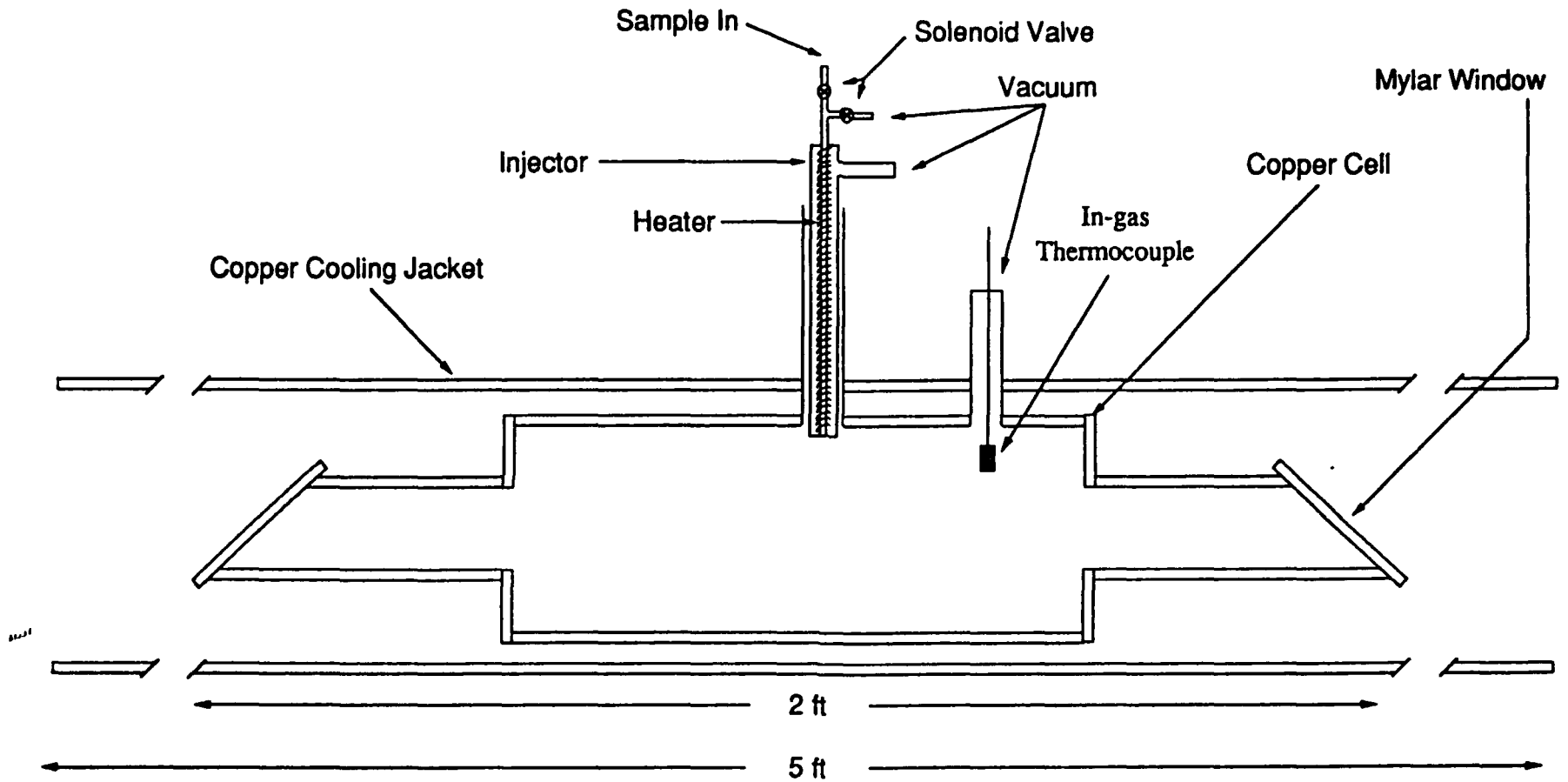
a. Absolute uncertainty estimated at ±10%. Relative uncertainty estimated at ±5%.

TABLE II

HDO Pressure Broadening Parameters.[a,b]

		$2_{1,1}$-$2_{1,2}$	$3_{1,2}$-$2_{2,1}$	$7_{3,4}$-$6_{4,3}$
Helium	n	0.50(5)	0.52(3)	0.50(5)
	γ_0	0.78(1)	0.74(1)	0.52(1)
Hydrogen	n	0.86(5)	0.81(2)	0.59(3)
	γ_0	3.9(1)	3.48(3)	2.51(4)
Oxygen	n	0.90(3)	0.96(2)	0.81(6)
	γ_0	2.71(5)	2.25(2)	1.58(5)
Nitrogen	n	0.77(1)	0.70(2)	0.67(5)
	γ_0	4.45(6)	4.21(4)	3.47(6)

a. γ in MHz/Torr.
b. Uncertainties are 1 standard deviation taken from fit.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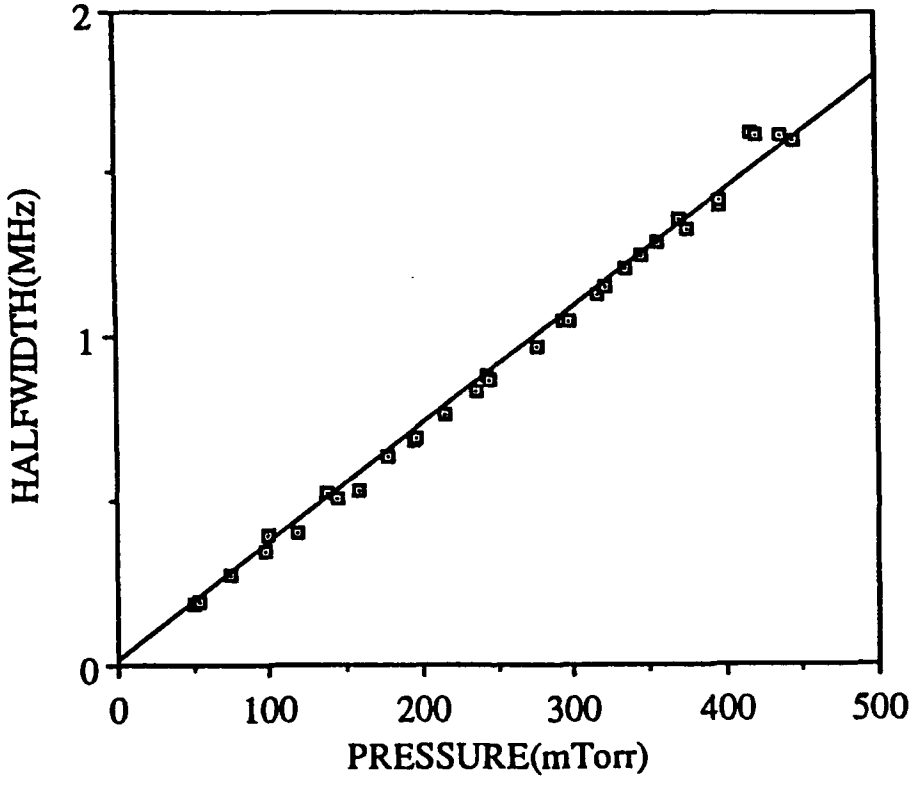
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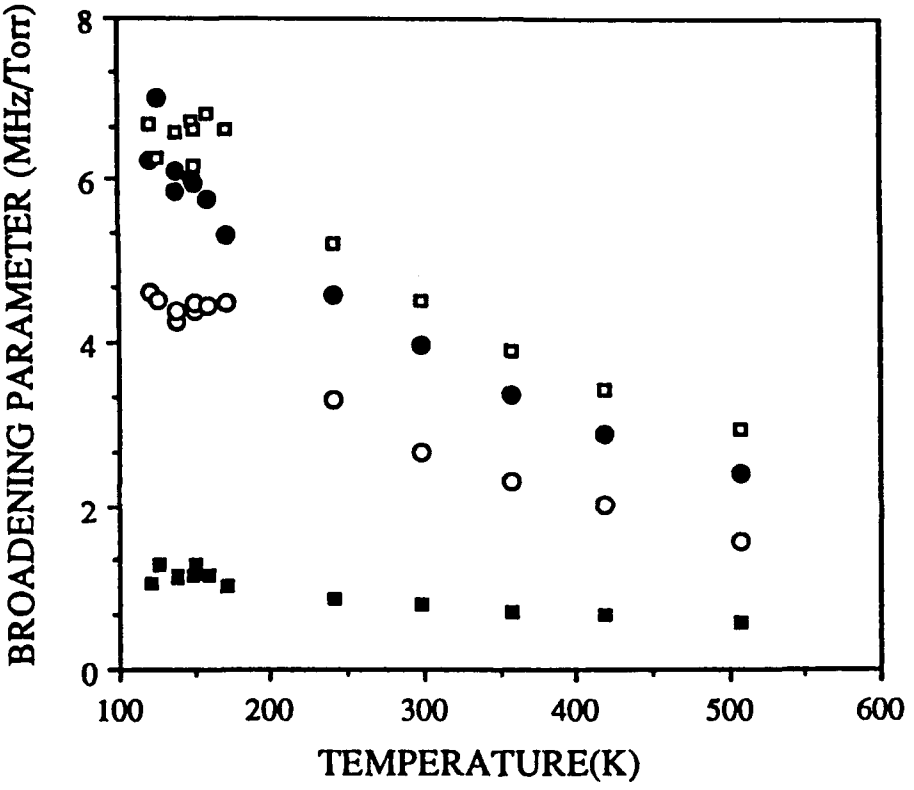
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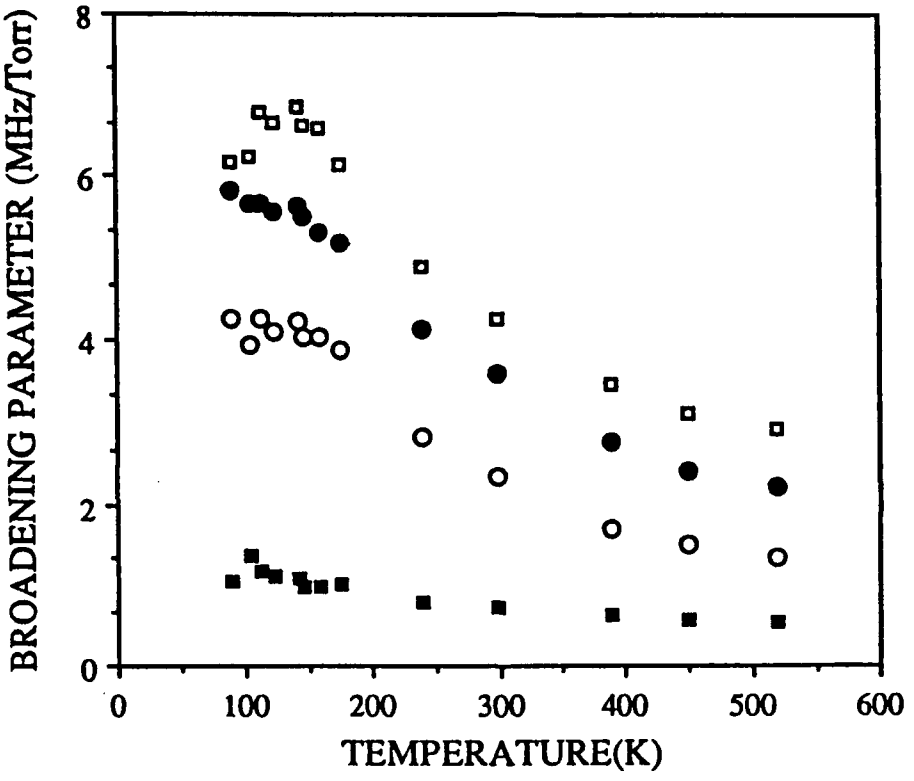
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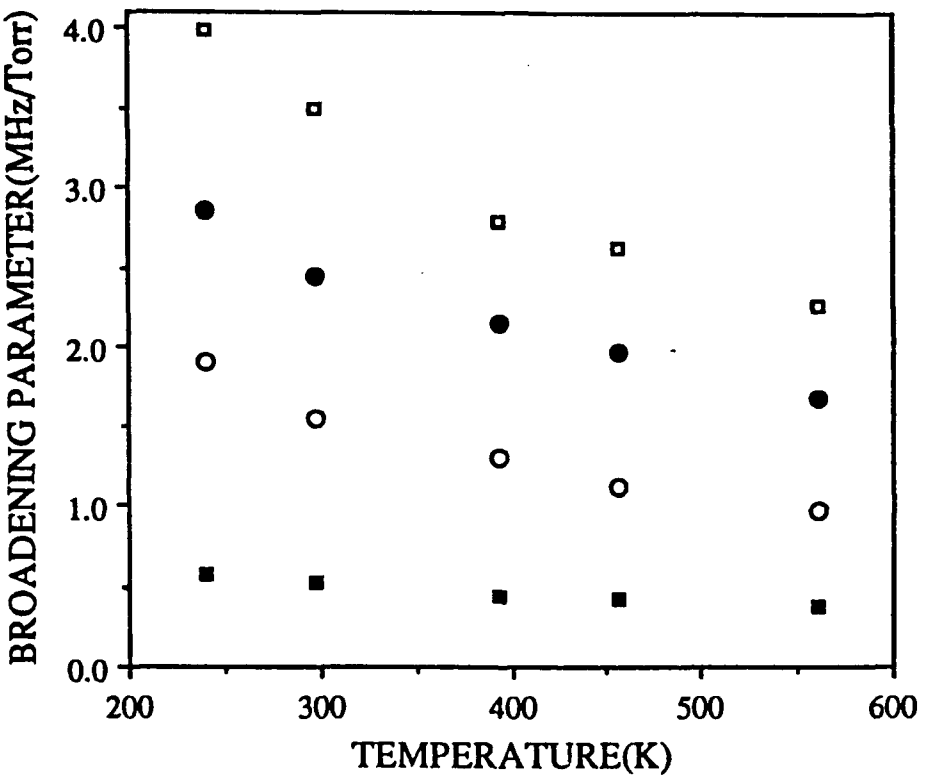
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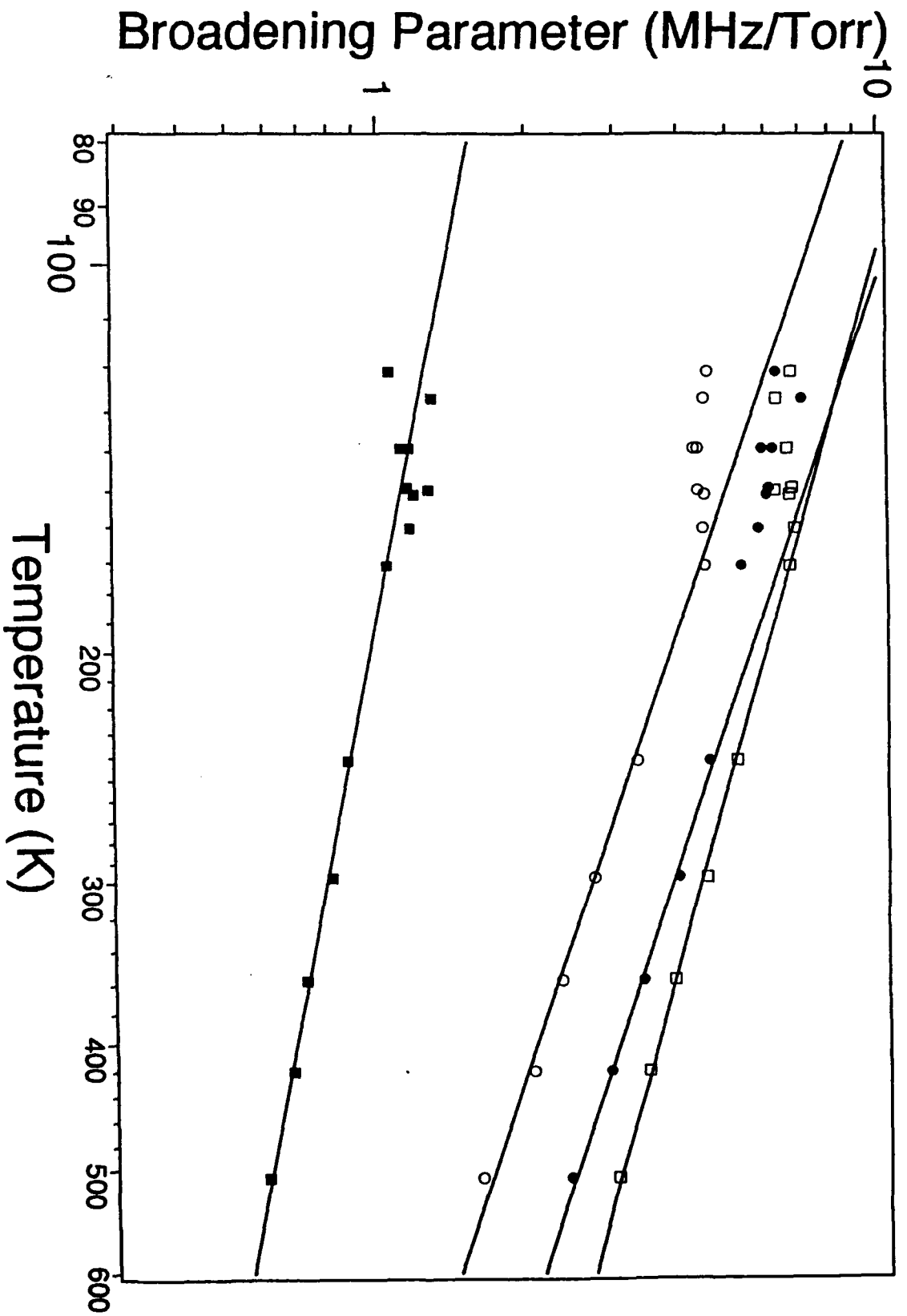
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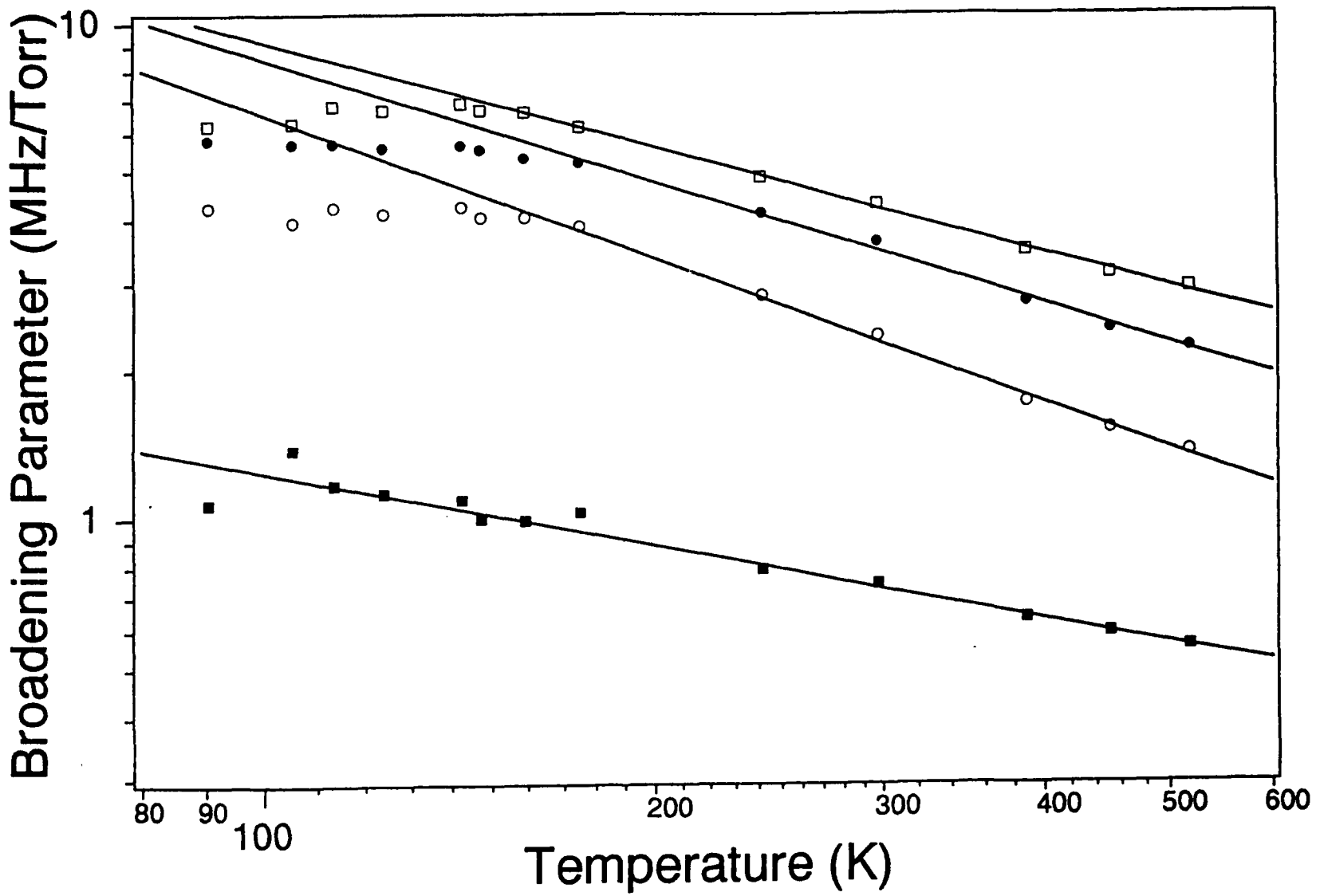
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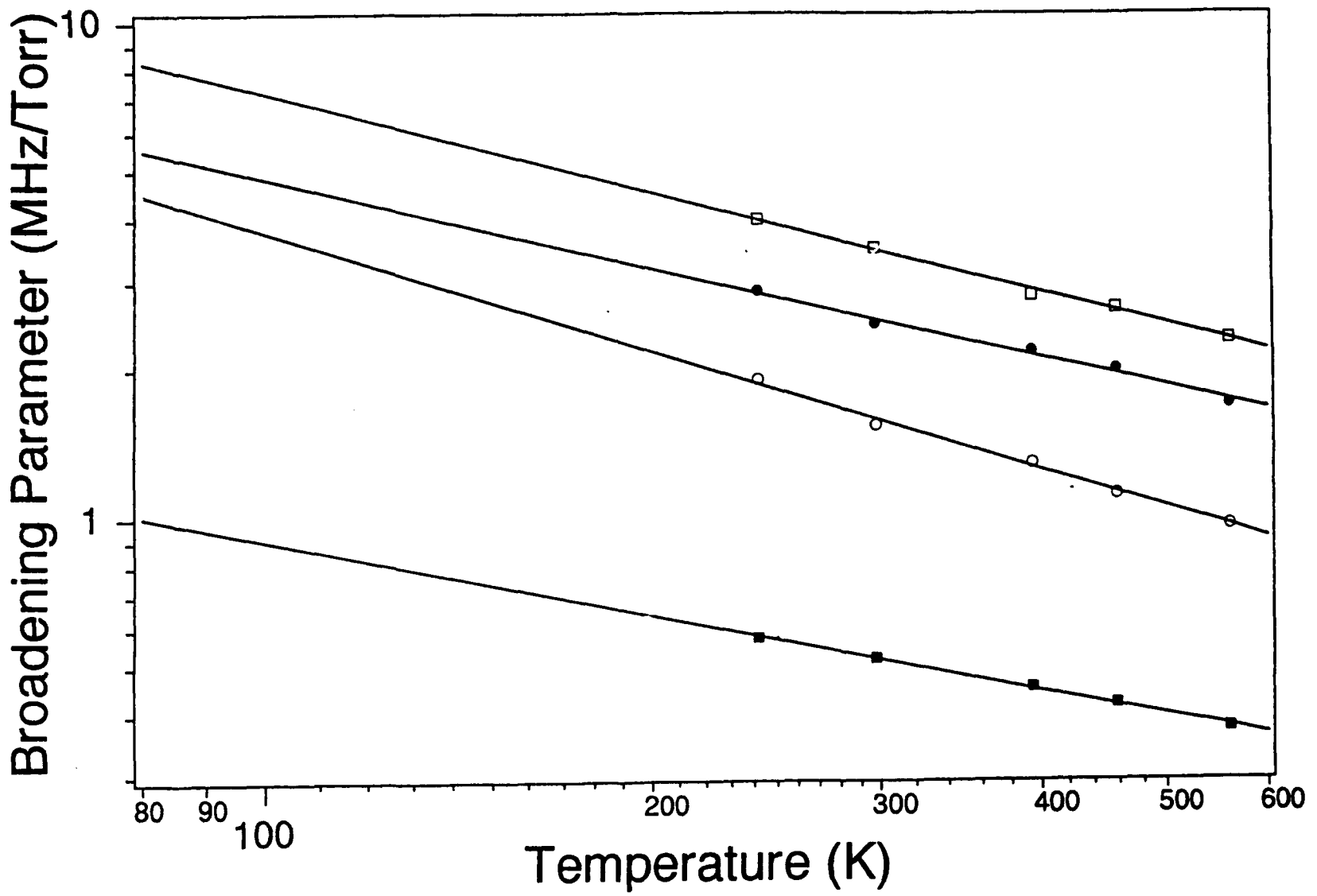
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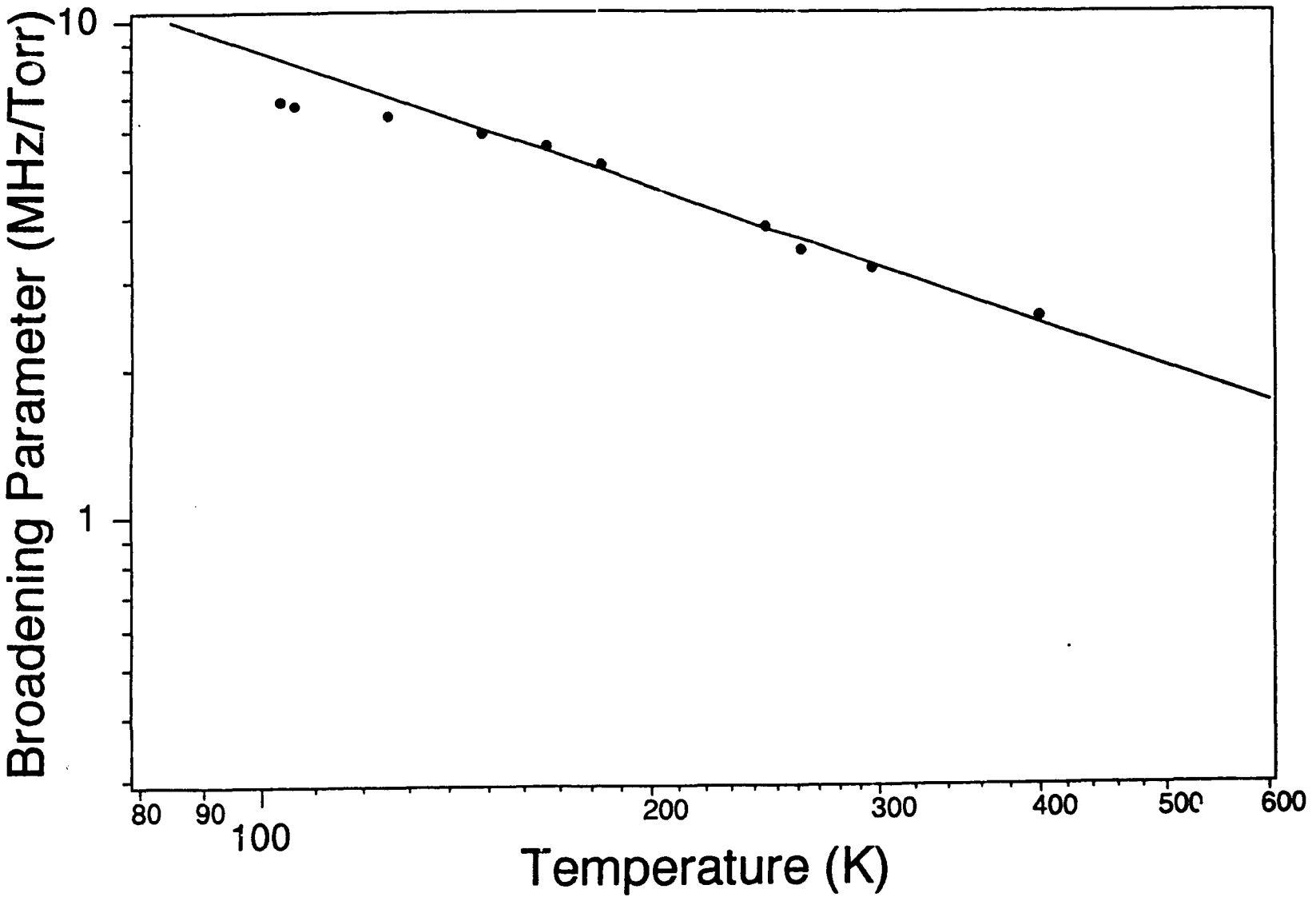
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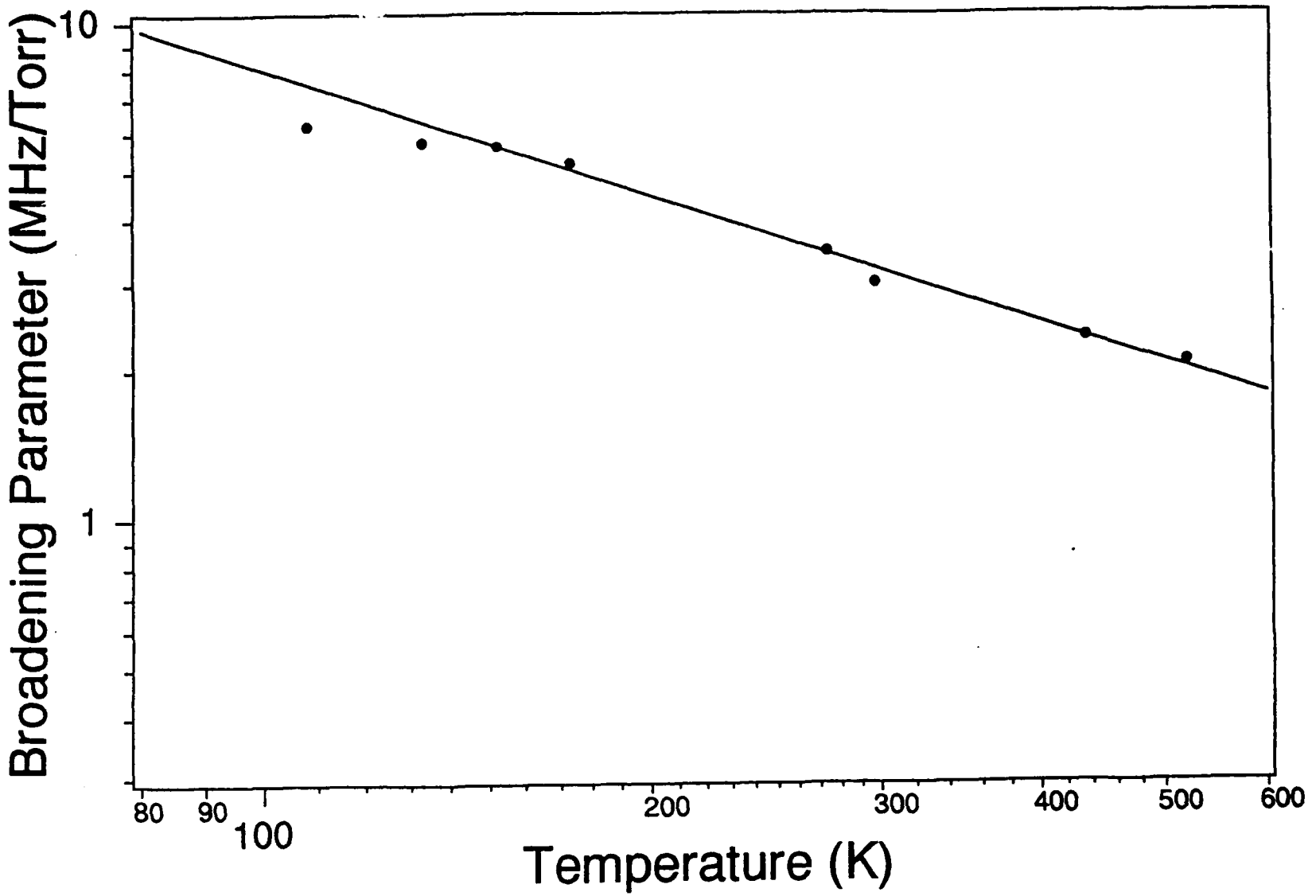
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